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DEVELOPMENT OF IMPROVED STRUCTURAL ADHESIVES

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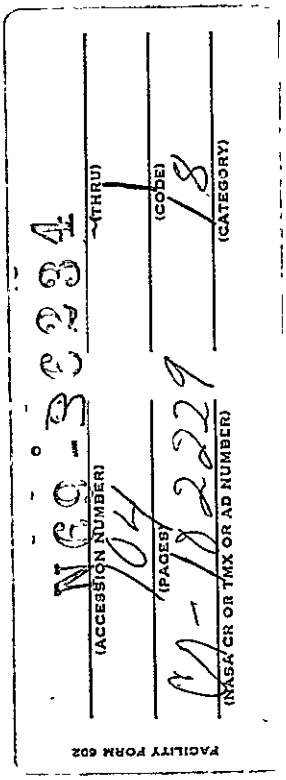

MONSANTO RESEARCH CORPORATION

A SUBSIDIARY OF MONSANTO COMPANY

DAYTON LABORATORY

DAYTON, OHIO 45407

DEVELOPMENT OF IMPROVED STRUCTURAL ADHESIVES

by

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Prepared under Contract No. NAS8-20406
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ABSTRACT

This report consists of the results of investigations directed toward development of an improved adhesive for bonding aluminum over the temperature range of -253°C to +150°C. Three polymer systems - polyurethanes, poly-2-oxazolidones and epoxies - were investigated.

An investigation of the effect of diisocyanate structure on strength properties and pot life of polyurethane adhesives has resulted in the development of an adhesive system to meet the goals of this contract. Tensile shear strengths from -269°C to +150°C and T-peel strengths from -196°C to +150°C either meet or exceed target values. The pot life of the formulation is in excess of two hours (target value). The diisocyanate which resulted in this development is 2,6-diethyl-*p*-phenylene diisocyanate.

The adhesive is a 4,4'-methylenebis(*o*-chloroaniline)-cured 2,6-diethyl-*p*-phenylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol containing 0.5% γ-glycidoxypropyltrimethoxysilane additive. Adequate adhesive strengths have been obtained using several aluminum surface treatments with and without primer. Poor prepolymer stability appears to be the major shortcoming of the system.

An investigation of various poly-2-oxazolidones as adhesives has shown that only low 150°C strengths can be expected with systems capable of meeting low temperature strength goals. Several improved catalysts were found for poly-2-oxazolidone formation.

A limited investigation of modified epoxy resins designed to improve T-peel strengths was carried out without showing much promise of success.

FOREWORD

This report was prepared by Monsanto Research Corporation, Dayton Laboratory, under Contract No. NAS8-20406, "Development of Improved Structural Adhesives", for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Propulsion and Vehicle Engineering Laboratory, Materials Division of the George C. Marshall Space Flight Center with Dr. William E. Hill acting as project manager.

The work was performed at the Dayton Laboratory of Monsanto Research Corporation by Dr. D. G. Glasgow, project leader, Mr. C. E. McClung, Mr. A. E. Follett, and Mr. R. P. Quill.

The authors are indebted to Dr. J. M. Butler for his many helpful suggestions and stimulating discussions. Also, the capable assistance of Mr. C. E. Lowe, who prepared the adhesive samples, and Mr. N. W. Mott, Mr. G. L. Wentz, Mr. F. E. Stewart, Mrs. C. Fritsch, and Mrs. R. J. Burton who conducted the physical tests, is appreciated.

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I. SUMMARY

A. POLYURETHANE ADHESIVES

An investigation of the effect of diisocyanate structure on adhesive strengths and pot lives of polyurethane adhesives was conducted. A total of twelve diisocyanates was prepared and tested in adhesive formulations. The best diisocyanate structure found, in terms of bond strength and pot life of the corresponding adhesive, was 2,6-diethyl-*p*-phenylene diisocyanate.

Investigation of adhesives based on 2,6-diethyl-*p*-phenylene diisocyanate resulted in the development of a formluation whose strength properties and pot life meet or exceed the goals of this contract. This adhesive is a 4,4'-methylenebis(*o*-chloroaniline) (MOCA)-cured 2,6-diethyl-*p*-phenylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol containing 0.5% γ-glycidoxypropyltrimethoxysilane. The properties of this adhesive are shown below in comparison with the contract goals and the prior art.

PROPERTY	TEMP. °C	CONTRACT GOALS	DEVELOPED ADHESIVE	PRIOR ART
Tensile Shear Strength, psi	-253	4000	4400-6250	
	-196		>6000	>6700
	+150	1500	1570-1780	410
T-Peel Strength, piw	-196	20	20-27	44
	+150	20	18-26	66
Pot Life, min		120	>120	∿60

The data for the developed adhesive are a composite of five determinations, each determination using a different combination of aluminum surface preparation and primer. These data represent the best and most reproducible obtained on this particular adhesive system.

The developed adhesive system has been optimized with respect to the cure cycle. A cure of 24 hours at room temperature followed by 24 hours at 110°C was found to be best.

An evaluation of several aluminum surface preparations showed that the usual chromic acid etch is probably as good as any, provided other variables are constant. The other surface treatments tested that appeared to be equally good were chromic acid etch followed by a ferrous sulfate rinse and an alkali treatment followed by the chromic acid-ferrous sulfate treatment. Essentially equivalent

strengths have been obtained using either N-(trimethoxysilylpropyl)-ethylenediamine primer, hydrolyzed γ-glycidoxypropyltrimethoxysilane primer or no primer.

The major shortcoming of this adhesive, at its present stage of development, is the stability of the prepolymer. A definite correlation between decreasing bond strengths and number of times the prepolymer was exposed to the atmosphere has been shown. This correlation seemingly does not exist with the 2,4-tolylene diisocyanate based adhesives handled in the same manner.

A series of 2,6-diethyl-*p*-phenylene diisocyanate-based adhesives were prepared to evaluate the effect of variations in the polyoxytetramethylene glycol molecular weight between 620 and 1000. This study showed that, in general, increasing the glycol molecular weight decreased the -196°C and 150°C strengths. Some adhesives were prepared which met the contract goals, although reproducibility was very poor.

A second adhesive system that showed good promise on limited data was a MOCA-cured 3,5-diethyl-4,4'-diisocyanatodiphenylmethane-terminated 1000 molecular weight polyoxytetramethylene glycol. Only the 150°C tensile shear strengths were below target values.

Aromatic diamine curing agents were studied in an attempt to find a curing agent to replace MOCA. The results indicated that the curing agents, a total of eighteen, studied could not give the desired bond strengths, particularly at 150°C.

An attempt was made to increase the -196°C T-peel strength of polyurethane adhesives by the use of fillers. Only decreased T-peel strengths and shorter pot lives were obtained.

A series of scanning electron micrographs was taken of the aluminum surfaces, resulting from various chemical treatments. No correlation of gross physical structure with bond strength was found. The micrographs did porvide some insight into the manner in which these chemical treatments affect the surface.

B. POLY-2-OXAZOLIDONE ADHESIVES

The poly-2-oxazolidones, formed from isocyanates and epoxides, were evaluated for their potential use as adhesives. During this evaluation of series of improved catalysts for the formation of the 2-oxazolidone ring was found. Tetrabutylphosphonium chloride was the most effective catalyst found.

A structure-property study of the isocyanates and epoxides used to prepare the poly-2-oxazolidones showed that only low 150°C strengths could be expected from polymers that had sufficient -196°C strength. The pot lives of these adhesive formulations are well in excess of the target value of two hours.

C. EPOXY ADHESIVES

A limited study of modified epoxy resins designed to improve T-peel strength was carried out. Several materials were synthesized, but the adhesive strengths obtained were not sufficient to warrant an extensive program in this area.

II. INTRODUCTION

The objective of this research program is the development of an adhesive for aluminum which has improved properties over the range of -253°C to +150°C. Properties sought are a minimum T-peel strength of 20 pounds per inch width (piw) at -196°C and +150°C, and minimum lap shear tensile strengths of 4000 psi and 1500 psi at -253°C and +150°C, respectively. Additional objectives are: a cure temperature under 120°C (preferably 25-30°C); bonding pressures of 5-10 psi; a minimum pot life of 120 minutes; and simple handling, assembling, and curing processes.

This year's work encompassed the study of three polymer systems; the polyurethanes, poly-2-oxazolidones and epoxies. The major emphasis was placed on investigation of the polyurethane adhesives. The program has covered the following principal phases:

1. A study of the effect of diisocyanate structure on the bond strength and pot life of polyurethane adhesives.

2. Optimization of the best polyurethane adhesive system with respect to cure cycle and aluminum surface preparation.

3. A study of the effects of structure on properties of poly-2-oxazolidone adhesives.

4. Investigation of some modified epoxy structures to improve T-peel strengths.

This report covers the work performed during the period July 1967 to December 1968.

III. RESULTS AND DISCUSSION

A. POLYURETHANE ADHESIVES

It was established during the first year of this contract that the polyurethane adhesives that offer the best chance for successfully fulfilling the contract goals are those based on the lower molecular weight (620 or 1000) polyoxytetramethylene glycols. In addition, it was shown that aromatic diisocyanates and aromatic amine curing agents were necessary if the desired high-temperature strengths were to be realized. Some adhesives prepared from these materials exhibited tensile shear and T-peel strengths over the temperature range of -196°C to +150°C which nearly met the contract goals. The major shortcoming of these adhesives was their short pot lives. Since the reaction rate of the isocyanate with the amine governs the pot life of the adhesive, modification of these functions to lower the reaction rate was a major objective of this second year's work. The result was the development of an adhesive that meets the contract goals of pot life and adhesive strength from -269°C to +150°C.

The discussion of this effort can be divided into three general areas:

1. preparation and testing of diisocyanates expected to exhibit slow rates of reaction

2. preparation and testing of aromatic diamine curing agents which also should be relatively unreactive

3. physical methods for lengthening the pot life of the previously developed adhesives.

The discussion of each of these investigations along with some minor studies is given in the following sections.

The tensile shear and T-peel specimens used in this program were prepared from 0.064 in. and 0.032 in. or 0.025 in. Alclad Aluminum 2014-T6 (Federal Specification QQ-A-255) respectively as discussed in the Experimental Section. The change from 0.032 in. to 0.025 in. aluminum occurred, because we were no longer able to procure 0.032 in. aluminum in small quantities. Three experiments were run using both thicknesses and the results indicated that T-peel strengths obtained on 0.025 in. aluminum were slightly lower.

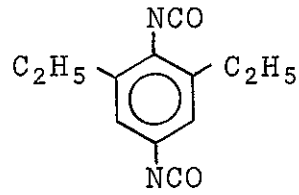
After preparation the adhesive test specimens were stored at 23°C and 50% RH for one to seven days prior to testing. The strength values given in this report are the average of three individual values. For the most part, the consistency of the results within a given set was good. Individual values were eliminated only when they differed

significantly from other values in a given set or when visual inspection of the specimen after testing showed a starved bond line.

The 4,4'-methylenebis(*o*-chloroaniline) (MOCA) used in this study was purified to remove *o*-chloroaniline and water.

One objective of this contract was to obtain a tensile shear strength of at least 4000 psi at -253°C, i.e., the boiling point of liquid hydrogen. For safety reasons the low temperature tests were carried out in liquid helium (b.p. -269°C). It was assumed that any adhesive which had tensile shear strength in excess of 4000 psi at both -269°C and -196°C would also have more than 4000 psi tensile shear strength at -253°C.

1. 2,6-Diethyl-*p*-phenylene Diisocyanate-Based Adhesives. Twelve diisocyanates, which had not previously been studied for use in cryogenic adhesives, were prepared and tested in adhesive formulations. The formulations that gave the best combination of pot life, processability and adhesive strengths were those based on 2,6-diethyl-*p*-phenylene diisocyanate,



Therefore, this diisocyanate was selected for further investigation. The result was the development of an adhesive formulation which fulfilled the contract goals of tensile shear strength (-269°C to +150°C) T-peel strength (-196°C to +150°C) and pot life (2 hours). In addition, it can be processed in the same manner as presently available polyurethane adhesives. The adhesive is a 4,4'-methylenebis(*o*-chloroaniline) (MOCA)-cured 2,6-diethyl-*p*-phenylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol containing 0.5% γ-glycidoxypropyltrimethoxysilane. The aluminum substrate can be etched and primed in a variety of combinations.

The developed adhesive has a pot life of at least two hours as measured using a viscosity versus time technique discussed in the Experimental Section. It was noted, however, that even when the viscosity of the 2,6-diethyl-*p*-phenylene diisocyanate-based adhesive was eight times greater than the viscosity taken as the end point of pot life, the adhesive could still be easily spread, i.e., gelation had not occurred. This is probably due to the hindered isocyanate function which reacts with amine to form linear polymer but does not form allophanates or biurets readily enough to introduce crosslinking.

at least in the early stages of reaction. If this assumption is correct, the working life available with this adhesive will be even greater than estimated.

The following subsections are discussions of the various individual studies which, when combined, resulted in development of the above adhesive. These individual studies serve to help define the limitations which can be expected with variations in adhesive formulation and curing conditions.

a. Effect of Cure Conditions. Although the initial study of 2,6-diethyl-*p*-phenylene diisocyanate-based adhesives showed promise in terms of pot life, it was soon obvious that a cure cycle other than the one used with 2,4-tolylene diisocyanate-based adhesives was needed. Therefore, the effects of various cure temperatures and times on adhesive strength was determined. Cure temperatures of 75°, 90°, 100°, 110° and 120°C and cure times of 24, 48, 72, and 96 hours were used following a period of 24 hours at room temperature. The data obtained with 620 molecular weight polyoxytetramethylene glycol-based adhesives are given in Table 1.

Examination of the data in Table 1 shows that a cure cycle of 24 hours at room temperature followed by 24 hours at 110°C results in the best adhesive strengths. Cure temperatures of less than 110°C did not result in adequate -196°C T-peel strengths. Also a cure temperature of 120°C did not result in any improvement in strength values. In addition, adhesives cured at 110°C exhibited only adhesive failure during the 150°C T-peel tests. Lower cure temperatures usually resulted in the occurrence of some cohesive failure in this test. This indicated that 110°C was needed to obtain full cure of the polymer. As a result of this study a cycle of 24 hours at room temperature followed by 24 hours at 110°C was used to cure the majority of the 2,6-diethyl-*p*-phenylene diisocyanate-based adhesives used in this program.

b. Effect of Substrate Surface Treatments. Proper preparation of the substrate is a very important step in adhesive bonding. The surface must not have present any mechanically weak layers or extraneous material, since these would result in a weak interfacial bond and low adhesive strength. Preparation of a metal surface is often accomplished by chemical etching. In addition, it is sometimes necessary to apply a primer once the substrate surface has been adequately prepared. This is especially true in the bonding of aluminum with polyurethanes. A discussion of the effects of various primers and priming methods is given in Section A.1.d. Following is a discussion of the effect of several surface treatments on the adhesive strengths of MOCA-cured 2,6-diethyl-*p*-phenylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycols. These surfaces were also examined with a scanning electron microscope and the results are discussed in Section A.9.

Table 1

EVALUATION OF CURING CONDITIONS

FOR 2,6-DIETHYL-*p*-PHENYLENE DIISOCYANATE-BASED ADHESIVES[1]

SAMPLE NO.	PREPOLYMER % NCO	PERCENT A-187[2]	CURE CONDITIONS TEMP., °C	CURE CONDITIONS TIME, hr	TENSILE SHEAR STRENGTH, psi -196°C	TENSILE SHEAR STRENGTH, psi 23°C	TENSILE SHEAR STRENGTH, psi 150°C	T-PEEL STRENGTH, piw[3] -196°C	T-PEEL STRENGTH, piw[3] 23°C	T-PEEL STRENGTH, piw[3] 150°C
71445	7.60	0.5	75	24	2500	4700	1090	9	34	12
81570	7.60	0.5	75	72	5350		1520			
81610	7.04	0.5	75	72	3000	4250	1170	4	11	8
81630	7.04	--	75	72		4450	1290		17	14
90751A	7.04	1.0	75	48			1070			4
B	7.04	1.0	75	72			1100			7
C	7.04	1.0	75	96			1155			7
90754A	7.04	1.0	75	24						9
B	7.04	1.0	75	72	MF[4]			4		
C	7.04	1.0	75	96	MF			8		
90752A	7.04	1.0	90	48			1425			20
B	7.04	1.0	90	72			1480			44
C	7.04	1.0	90	96			1495			47
90755A	7.04	1.0	90	24						11
B	7.04	1.0	90	48	MF			8		
C	7.04	1.0	90	72	MF			10		
90770	7.04	1.0	90	72	MF	5100	1540	12	36	30
90797	8.07	1.0	90	72	MF	MF	1610	14	34	32
90827A	7.99	1.0	100	24			1370			
90786A	7.04	1.0	110	24			>2000	21		
B	7.04	1.0	110	48			>2000	19		
C	7.04	1.0	110	72			>2000	17		
90800	8.07	1.0	110	24	MF	5350	1910	16	32	39
90827	8.07	1.0	120	24	4480	5370	1830	16	25	16

[1]Adhesives were MOCA-cured 620 molecular weight polyoxytetramethylene glycol-based prepolymers, (NCO:NH_2 of 1.05). Aluminum was etched in standard sulfuric acid-sodium dichromate bath at 70°C for ten minutes. Aluminum primed with 1.0% ethanolic solution of N-(trimethoxysilylpropyl)ethylenediamine

[2]A-187, γ-glycidoxypropyltrimethoxysilane

[3]T-peel strengths determined on 0.032" aluminum

[4]MF, metal failure at pin hole grip

The most widely used surface preparation for aluminum and the one used almost exclusively in this study is a chromic acid etch at 70°C for 10 minutes. In the latter stages of this program a variation of this method was reported by H. N. Varizani (Ref. 1). In Varizani's method the aluminum is immersed in an alkaline cleaning bath after degreasing. From the alkaline bath it is etched in the standard chromic acid bath. Immediately after removal from the chromic acid bath it is immersed in a 0.1 *N* ferrous sulfate bath for 30 seconds at room temperature. After this treatment the aluminum is thoroughly rinsed with distilled water and dried as usual. The details of this method are given in the Experimental Section. According to Dr. Varizani, the ferrous sulfate treatment prevents excessive hydration of the surface and also prevents sealing. This method was reported to also increase the durability of bonds under stress when an epoxy adhesive was used.

The above method was used with the developed polyurethane adhesive. The same method with elimination of the alkaline treatment was also tried. Several combinations of the three surface treatments (chromic acid, chromic acid-ferrous sulfate and alkali-chromic acid-ferrous sulfate) with two primers and without primer were tested. The results of this work are given in Table 2.

The initial results obtained with the ferrous sulfate treatment both with and without prior use of the alkali bath resulted in adhesive strengths in excess of contract goals from -196°C to +150°C. This represents an improvement in strength values compared to those obtained when only a chromic acid etch was used. This is shown by comparing Samples 96626, 96633 and 96632.

By using another lot of prepolymer and the alkali-chromic acid-ferrous sulfate treatment, low strengths resulted (Sample 96648). These low strengths more likely reflect the stability of the prepolymer (as discussed in Section A.1.c) rather than an inadequate surface treatment.

Using a freshly prepared prepolymer, a series of sixteen experiments were run over a period of fifteen days. The three surface preparations were used with two primers, N-(trimethoxysilylpropyl)ethylenediamine (A-1120) and hydrolyzed γ-glycidoxypropyltrimethoxysilane (A-187) and without primer. Only two of the nine possible combinations were not tested.

Using this new lot of prepolymer, the hydrolyzed A-187 primer and the chromic acid surface treatment resulted in an adhesive whose strengths exceeded all the goals from -269°C to +150°C and one which lacked only sufficient -196°C T-peel strength (Samples 103,805 and 103,822, Table 2). Use of the ferrous sulfate rinse with the above combination

resulted in three adhesives with the desired adhesive strengths and two which lacked only -196°C T-peel strength (Samples 103,810 to 103,825, Table 2). When the same prepolymer and primer were used with the alkali-chromic acid-ferrous sulfate treatment one of three adhesives had the desired strengths and the other two lacked only -196°C T-peel strength (Samples 103,809 to 103,819, Table 2). Since only cohesive failure occurs in the -196°C T-peel test, these strengths reflect polymer strength rather than the strength of the polymer-aluminum bond.

Adhesives were prepared again using the same prepolymer but with the A-1120 primer and two surface treatments. With the chromic acid-ferrous sulfate treatment, only the 150°C T-peel strength was below target values (Sample 103,824). All the desired strength values including -269°C tensile shear strength were obtained when the alkali-chromic acid-ferrous sulfate treatment was employed (Sample 103,808).

The use of no primer was tested with two surface treatments and three additive levels. The additive used was γ-glycidoxypropyltrimethoxysilane. With 0.5% additive and the chromic acid-ferrous sulfate treatment only 150°C T-peel strength was below target values (Sample 103,817) while all the desired strengths were obtained with the alkali-chromic acid-ferrous sulfate treatment (Sample 103,816, Table 2). Use of 0.75% additive (Sample 103,806) and 1.0% additive (Sample 103,807) with the alkali-chromic acid-ferrous sulfate treatment resulted in the desired adhesive strengths being obtained including -269°C tensile shear strength.

The data in Table 2 show the excellent strengths to be expected with this new adhesive. The last group of sixteen experiments just discussed were especially significant, since they indicated that the desired adhesive strengths could be obtained in a variety of ways with the developed adhesive. Evidently the chromic acid etch is sufficient assuming other variables, *e.g.*, primer, prepolymer conditions, are optimum.

The fact that the desired strengths were obtained without primer, *i.e.*, using additive only, is particularly interesting as it would eliminate one processing step. Also, the excellent strengths obtained with the hydrolyzed A-187 primer were significant. Data by Holland (Ref. 2) and Hill (Ref. 3) show that this primer is desirable for strength retention in humid atmospheres.

As the data in the next section will indicate, it is important that the prepolymer be carefully maintained under dry nitrogen. In the sixteen experiments, the bottle containing the prepolymer was opened a total of only eight times in the sixteen day period thus limiting exposure.

Table 2

EVALUATION OF ALUMINUM SURFACE TREATMENTS[1]

SAMPLE NO.	PREPOLYMER % NCO	PERCENT ADDITIVE[2]	PRIMER	ALUMINUM SURFACE TREATMENT			TENSILE SHEAR STRENGTH, psi				T-PEEL STRENGTH, piw[7]		
				ALKALI[3]	ACID[4]	$FeSO_4$[5]	-269°C[6]	-196°C	23°C	150°C	-196°C	23°C	150°C
96626	8.09	0.5	A-1120[8]	--	XX	--		3350	5180	1470	18	26	36
96633	8.09	0.5	A-1120	--	XX	XX		5330	5300	1720	23	42	22
96632	8.09	0 5	A-1120	XX	XX	XX		5590	5200	1770	25	45	30
96648	7 79	0.5	Hyd[9]	XX	XX	XX		1880	5100	840	7	21	6
103805	7.75	0.5	Hyd	--	XX	--	4450	5120	5580	1780	21	27	21
103822	7.75	0.5	Hyd	--	XX	--		MF[10]	5480	1720	17	27	28
103810	7.75	0.5	Hyd	--	XX	XX	4400	MF	5280	1650	20	25	26
103820	7.75	0.5	Hyd	--	XX	XX		MF	5270	1640	25	25	23
103821	7.75	0.5	Hyd	--	XX	XX		4730	5380	1810	18	23	25
103823	7.75	0.5	Hyd	--	XX	XX		5730	5120	1770	24	27	20
103825	7.75	0.5	Hyd	--	XX	XX		5700	5100	1680	17	22	21
103809	7.75	0.5	Hyd	XX	XX	XX		5170	5200	1600	17	28	24
103811	7.75	0.5	Hyd	XX	XX	XX		4930	5320	1530	14	34	27
103819	7.75	0.5	Hyd	XX	XX	XX		MF	5200	1660	22	32	25
103824	7.75	0.5	A-1120	--	XX	XX		5850	5200	1580	24	30	19
103808	7.75	0.5	A-1120	XX	XX	XX	6150	MF	5520	1780	20	27	22
103817	7.75	0.5	--	--	XX	XX	5600	MF	5250	1630	23	23	18
103816	7.75	0.5	--	XX	XX	XX		MF	5380	1760	25	34	22
103806	7.75	0.75	--	XX	XX	XX		5350	5250	1630	22	32	20
103807	7.75	1.0	--	XX	XX	XX	6250	MF	5430	1570	27	28	20

[1]Adhesives were MOCA-cured 2,6-diethyl-p-phenylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycols ($NCO \cdot NH_2$ of 1.05). Cure was 24 hours at room temperature followed by 24 hours at 110°C

[2]Additive was γ-glycidoxypropyltrimethoxysilane, either Z-6040 (Dow Chemical Co.) or A-187 (Union Carbide Co.)

[3]Aluminum was alkaline detergent cleaned at 70°C for 10 minutes in a bath composed of 33.6 g sodium hydroxide, 56.3 g sodium pyrophosphate and 67.2 g sodium metasilicate in 2850 ml water. Panels were rinsed in tap water followed by deionized water. XX indicates use of this treatment.

[4]Aluminum was etched at 70°C for 10 minutes in a bath composed of 10 parts sodium dichromate dihydrate and 100 parts concentrated sulfuric acid in 300 parts water. Panels were rinsed in tap water followed by deionized water. XX indicates use of this treatment.

[5]Aluminum was removed from the chromic acid bath and immersed for 30 seconds in a 0.1N ferrous sulfate bath at room temperature. Panels were rinsed in tap water followed by deionized water. XX indicates use of this treatment.

[6]Each number represents a single sample

[7]T-peel strengths determined on 0.025" aluminum

[8]A-1120, N-(trimethoxysilylpropyl)ethylenediamine (Union Carbide Co.). A 1.0% solution in stock etnanol (0.2% water) was used as the primer.

[9]Hyd, hydrolyzed γ-glycidoxypropyltrimethoxysilane. Primer prepared by mixing 2.2 g of a 10% solution of the silane in 1% aqueous acetic acid with 100 g of methanol

[10]MF, metal failure at pin hole grip

c. Prepolymer Stability. It is well known that isocyanates react with moisture and therefore must be stored under dry conditions. In working with 2,4-tolylene diisocyanate-based prepolymers a technique involving opening containers and transferring prepolymer under a blanket of dry nitrogen was used. This technique appeared to be adequate, and no correlation of decreasing bond strength with number of times the prepolymer container was opened could be found. Therefore, this technique was used with all the new diisocyanate-based prepolymers. However, the technique did not appear to be adequate as shown by the data in Table 3.

Table 3 lists the initial strength values obtained with several lots of 2,6-diethyl-*p*-phenylene diisocyanate-based prepolymer adhesives along with selected values obtained subsequently. In each case where the data was available a decrease in strength with time was noted. The decrease in strength was most noticeable in the -196°C tensile shear strength and the -196°C and +150°C T-peel strength values.

The last three samples in Table 3 are the most significant, as they show that the strength decrease reflects exposure to air rather than simply prepolymer age. Sample 96642 represents the initial use of this particular prepolymer. Sample 103,813 represents the values obtained after the prepolymer bottle had been opened eight times. Sample 103,812 represents the values obtained with prepolymer the same age as that used in Sample 103,813 but which had been exposed to air only once. These data indicate that much of the problem of poor reproducibility found in this program can be attributed to prepolymer instability.

The apparent decrease in prepolymer stability as compared to 2,4-tolylene diisocyanate-based prepolymers was surprising. Prepolymers based on 2,6-diethyl-*p*-phenylene diisocyanate would be expected to be more stable toward moisture due to the highly hindered isocyanate function. Instability due to other materials present in the atmosphere is not a problem with known isocyanates and would also not be expected to be a problem in this case. An adequate explanation would require further investigation.

d. Effect of Additives and Primers. Prior to finding that a considerable part of the problem in reproducibility was due to the prepolymer stability, the effects of additives and primers on bond strength of 2,6-diethyl-*p*-phenylene diisocyanate-based adhesives were given extensive study. Variables studied were: additive source and concentration and primer type and application method. In addition some variations of aluminum surface treatment, MOCA concentration and cure time were also included. The data are contained in

Table 3

EFFECT OF PREPOLYMER STABILITY ON BOND STRENGTH OF 2,6-DIETHYL-*p*-PHENYLENE DIISOCYANATE-BASED ADHESIVES[1]

SAMPLE NO.	PREPOLYMER % NCO	PERCENT ADDITIVE[2]	PRIMER	TENSILE SHEAR STRENGTH, psi			T-PEEL STRENGTH, piw[3]		
				-196°C	23°C	150°C	-196°C	23°C	150°C
90800	8.07	1.0	A-1120[4]	MF[5]	5350	1910	(16)	(32)	(39)
90848	7.46	0.5	A-1120	4280	5090	1520	(17)	(30)	(34)
96566	7.83	0.5	A-1120	5850	5490	1760	23	22	20
96587	7.83	0.5	A-1120	3700	5270	1450	14	24	22
96593	7.83	0.5	A-1120	2650	5990	970	11	23	19
96598	7.79	0.5	A-1120	MF	5470	1070	19	28	22
96607	7.79	0.5	A-1120	4980	5290	1270	19	26	24
96637	7.79	0.5	A-1120	2800	5400	1170	9	24	9
96618	8.09	0.5	A-1120	3830	5390	1570	21	25	20
96624B	8.09	0.5	A-1120	3820	5250	1280	15	27	26
103805	7.75	0.5	Hyd[6]	5120	5580	1780	21	27	21
10822	7.75	0.5	Hyd	MF	5400	1720	17	27	28
96642[7]	7.08	0.5	Hyd	5400	4500	1460	18	32	18
103813[7,8]	7.08	0.7	Hyd	1900	4670	810	8	30	3
103812[7,9]	7.08	0.7	Hyd	4400	4620	1300	15	32	16

[1]Adhesives were MOCA-cured prepolymers based on 620 molecular weight polyoxytetramethylene glycols except for Samples 96642, 103,813 and 103,812 (NCO:NH_2 of 1.05). Aluminum was etched in standard sulfuric acid-sodium dichromate bath at 70°C for ten minutes. Cure was done at 110°C for 24 hours

[2]Additive was γ-glycidoxypropyltrimethoxysilane, either Z-6040 (Dow Chemical Co.) or A-187 (Union Carbide Co.)

[3]T-peel strengths determined on 0.025" aluminum except for those in parenthesis which were determined on 0.032" aluminum

[4]A-1120, N-(trimethoxysilylpropyl)ethylenediamine, a 1.0% ethanolic solution

[5]MF, metal failure at pin hole grip

[6]Hyd, hydrolyzed γ-glycidoxypropyltrimethoxysilane. Primer prepared by mixing 2.2 g of a 10% solution of the silane in 1% aqueous acetic acid with 100 g of methanol

[7]Prepolymer based on 725 molecular weight glycol

[8]Prepolymer bottle opened eight times prior to use in this experiment

[9]Prepolymer for this experiment was stored separate from the main lot for two weeks prior to use

Tables 4 and 5. Section A.7 contains a discussion of similar work done with 2,4-tolylene diisocyanate-based adhesives.

The data in Table 4 were obtained using only one prepolymer. Samples 96598, 96637, 96638 and 96639 again show the effect of prepolymer instability. In addition, Samples 96637 and 96638 indicate that drying the ethanol used in the primer does not have any beneficial effect. Also, Samples 96638 and 96639 indicate that degassing of the prepolymer might not be necessary, a suggestion confirmed by the data of Holland and McLeod (Ref. 2).

The existence of a relationship between amounts of additive and primer used with a polyurethane adhesive was suggested by previous work on this contract (Ref. 4). This was again studied using the 2,6-diethyl-*p*-phenylene diisocyanate-based adhesives. Two primers, A-1120 and hydrolyzed A-187, were used in this study. The results, as given in Table 4, again indicate that with either primer an additive concentration of 0.5% is best. With no primer and 1.0% additive the adhesive strengths are comparable to those obtained with 1.0% additive and either primer.

The data in Table 5 were obtained as a result of checking a wide variety of minor variations in adhesive formulation and bonding procedures. Due to the effect of prepolymer stability, only comparisons based on data obtained with adhesives based on the same prepolymer and prepared at about the same time are considered valid.

Almost all of the investigations of adhesives based on 2,6-diethyl-*p*-phenylene diisocyanate used prepolymers which contained no unreacted diisocyanate. A prepolymer was prepared to determine if any beneficial effect could be obtained with a slight excess of isocyanate. This situation should result in polymers with increased strength at elevated temperatures due to the presence of more "hard segments". The prepolymer prepared for this study had an NCO content of 8.09, 0.1% above the theoretical value of 7.99. The shelf life of this prepolymer was not as good as those with NCO contents less than the theoretical value. A fine precipitate is noticeable on storage for a few weeks even though the bottle was unopened. The unhindered isocyanate function is evidently very sensitive to moisture and/or dimerization.

The MOCA-cured adhesives based on this prepolymer had adhesive strengths similar to those found previously using prepolymers of lower NCO content, particularly at 150°C. However, the -196°C tensile shear strengths were particularly low and only adhesive failure was observed. This was observed with either N-(trimethoxysilylpropyl)ethylenediamine (A-1120) primer, hydrolyzed γ-glycidoxypropyltrimethoxysilane (A-187) primer or no primer. T-peel strengths

Table 4

BOND STRENGTHS OF 2,6-DIETHYL-*p*-PHENYLENE DIISOCYANATE-TERMINATED 620 MOLECULAR WEIGHT POLYOXYTETRAMETHYLENE GLYCOL-BASED ADHESIVES: EFFECT OF ADDITIVE AND PRIMER VARIATIONS[1]

SAMPLE NO.	ADDITIVE	PERCENT ADDITIVE	PRIMER	TENSILE SHEAR STRENGTH, psi			T-PEEL STRENGTH, piw[2]		
				-196°C	23°C	150°C	-196°C	23°C	150°C
96598	A-187[3]	0.5	A-1120[4]	MF[5]	5470	1070	19	28	22
96637	Z-6040[6]	0.5	A-1120	2800	5400	1170	9	24	9
96638	Z-6040	0.5	A-1120d[7]	2560	5400	1110	8	21	14
96639[8]	Z-6040	0.5	A-1120d	3100	5600	1040	8	20	12
96607	A-187	0.5	A-1120	4980	5290	1270	19	26	24
96608	A-187	1.0	A-1120	3440	5430	1100	13	27	16
96601	A-187	1.0	A-1120	3700	5465	1170	13	29	22
96610	--	--	A-1120	4700	4650	900	17	21	17
96605	A-187	0.5	Hyd A-187[9]	5070	5350	1170	22	28	23
96612	A-187	0.5	Hyd Z-6040[10]	4880	4980	1130	22	27	25
96613	Z-6040	0.5	Hyd Z-6040	5050	5280	1340	21	25	30
96646	Z-6040	0.25	Hyd Z-6040	2000	5100	850	7	15	7
96643	Z-6040	0.5	Hyd Z-6040	2550	5200	1300	11	27	12
96647	Z-6040	0.75	Hyd Z-6040	2430	5330	1060	10	25	11
96606	A-187	1.0	Hyd A-187	3500	5330	1190	19	28	29
96609	--	--	Hyd A-187	4030	4520	910	18	22	25
96611	--	--	Hyd Z-6040	3580	4490	930	13	20	24
96600	A-187	1.0	--	3800	5400	1290	17	26	24
96615	A-187	1.0	--	3300	5200	1200	19	23	19
96614	Z-6040	1.0	--	2950	5200	1080	13	25	15

[1]Adhesives were MOCA-cured 2,6-diethyl-*p*-phenylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol (7.79% NCO). Aluminum was etched in standard sulfuric acid-sodium dichromate bath at 70°C for 10 minutes. Adhesives were cured at 110°C for 24 hours

[2]T-peel strengths were determined on 0.025" aluminum

[3]A-187, γ-glycidoxypropyltrimethoxysilane, Union Carbide Co.

[4]A-1120, N-(trimethoxysilylpropyl)ethylenediamine, a 1.0% ethanolic solution (0.02% water)

[5]MF, metal failure at pin hole grip

[6]Z-6040, γ-glycidoxypropyltrimethoxysilane, Dow Chemical Co.

[7]Primer prepared as in footnote 4 except ethanol dried over $CaSO_4$ was used

[8]Prepolymer was not degassed prior to addition of MOCA

[9]Hyd A-187, hydrolyzed A-187. Primer prepared by mixing 2.2 g of a 10% solution of A-187 in 1% aqueous acetic acid with 100 g of methanol. Primer applied by wiping

[10]Hyd Z-6040, hydrolyzed Z-6040. Primer prepared as in footnote 9

at -196°C and +150°C tensile shear strengths were usually close to or in excess of target values except when no primer was used. It appears that no significant beneficial effect is obtained with prepolymers containing slight excesses of diisocyanate.

A comparison of the adhesives prepared using the above prepolymer and a variety of minor variables (Samples 96618 to 96636) indicates that significant changes occur only when the primer is varied. This is shown by comparing Samples 96626 and 96625 which were prepared on the same day, thus eliminating the prepolymer stability variable.

The remaining data in Table 5 cannot be interpreted with any degree of reliability due to wide variations in number of times the prepolymer was exposed between experiments.

e. Effect of Glycol Molecular Weight. The first adhesive which met the contract goals was prepared from a 1:1 weight ratio of two prepolymers based on 620 and 1000 molecular weight polyoxytetramethylene glycols, respectively. The average glycol molecular weight of this mixture was about 775. We further investigated the effect of glycol molecular weight on adhesive strengths. In general, it would be expected that 150°C tensile shear strength would decrease and that the -196°C T-peel strength would increase with an increase in glycol molecular weight. Adhesives were prepared from prepolymers based on polyoxytetramethylene glycols of 725 molecular weight (Table 6), 810 molecular weight (Table 7), 1000 molecular weight (Table 7) and mixtures of the 620 and 1000 glycol molecular weight-based prepolymers (Tables 8 and 9).

The data in Tables 6 through 9 show that, in general, it was difficult to obtain the desired strengths with adhesives based on glycols of molecular weight greater than 620. Using the 725 molecular weight glycol-based adhesive, the contract goals were approached in one experiment. This was when the alkali-chromic acid-ferrous sulfate surface treatment was used (Samples 96649 of Table 6). Only 150°C T-peel strength was low.

A series of fourteen adhesives very similar to the type which passed the goals initially was prepared. Only the initial adhesive (Sample 90817, Table 8) meet all the goals, although two others closely approached the goals (Samples 90808 and 96570, Table 8).

The first adhesive with sufficient strength to pass all the strength goals (Sample 90817, Table 8) contained, what was probably, some high molecular weight prepolymer segments. The 1010 molecular weight polyoxytetramethylene glycol-based prepolymer used probably had a lower percent NCO than shown, *i.e.*, partial polymerization had occurre This prepolymer was visibly much more viscous than when originally

Table 5

BOND STRENGTHS OF 2,6-DIETHYL-*p*-PHENYLENE DIISOCYANATE-TERMINATED 620 MOLECULAR WEIGHT POLYOXYTETRAMETHYLENE GLYCOL-BASED ADHESIVES: EFFECT OF ADDITIVE AND PRIMER VARIATIONS[1]

SAMPLE NO.	PREPOLYMER % NCO	PERCENT A-187[2]	MOCA CONC[3]	CURE TIME, hr[4]	PRIMER	TENSILE SHEAR STRENGTH, psi			T-PEEL STRENGTH, piw[5]		
						-196°C	23°C	150°C	-196°C	23°C	150°C
90848	7.46	0.5	95%	24	A-1120[6]	4280	5090	1520	(17)	(30)	(34)
90832	8.07	--	95%	24	A-1120	5100	3570	1480	(19)	(21)	(25)
90838	8.07	1.5	95%	24	A-1120	3800	5200	1470	(14)	(29)	(31)
96618	8.09	0.5	95%	24	A-1120	3830	5390	1570	21	25	20
96619[7]	8.09	0.5	95%	24	A-1120	4050	5780	1420	21	22	21
96620[8]	8.09	0.5	95%	24	A-1120	3920	5490	1520	17	28	21
96624A[9]	8.09	0.5	95%	24	A-1120	2820	5250	1230	16	28	25
96624B[10]	8.09	0.5	95%	24	A-1120	3820	5250	1280	15	27	26
96626	8.09	0.5	95%	24	A-1120d[11]	3350	5180	1470	18	26	36
96625	8.09	0.5	95%	24	Hyd[12]	4600	5300	1540	19	21	21
96635	8.09	0.5	95%	24	--	1570	4500	450	6	31	9
96636	8.09	0.75	95%	24	--	2310	4000	930	6	50	13
96566	7.83	0.5	95%	24	A-1120	5850	5490	1760	23(31)	22(25)	20(24)
96587	7.83	0.5	95%	24	A-1120	3700	5270	1450	14	24	22
96590	7.83	0.5	95%	24	A-1120	1630	5030	890	7	19	14
96593	7.83	0.5	95%	24	A-1120	2650	5990	970	11	23	19
96599[13]	7.83	0.5	95%	24	A-1120	1650	4620	670	6	15	7
96571	7.83	0.5	90%	24	A-1120	4460	5400	1660	18	27	26
96573	7.83	0.5	100%	24	A-1120	4630	5360	1630	19	24	22
96588	7.83	0.5	100%	72	A-1120	1800	5000	850	6	12	--
96594	7.83	0.5	100%	72	A-1120	2270	4940	780	6	14	8

[1]Adhesives were MOCA-cured 2,6-diethyl-*p*-phenylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycols. Aluminum was etched in standard sulfuric acid-sodium dichromate bath at 70°C for ten minutes
[2]A-187, γ-glycidoxypropyltrimethoxysilane
[3]Percent of stoichiometric amount
[4]Cure was done at 110°C
[5]T-peel strengths determined on 0.025" aluminum except for those in parenthesis which were determined on 0.032" aluminum
[6]A-1120, N-(trimethoxysilylpropyl)ethylenediamine, a 1.0% ethanolic solution (0.02% water)
[7]Aluminum panels rinsed only in tap water after etching
[8]Aluminum panels rinsed only in distilled water after etching
[9]Aluminum etched in previously used chromic acid bath
[10]Aluminum etched in new chromic acid bath
[11]Primer prepared as in footnote 6 except ethanol dried over $CaSO_4$ was used
[12]Hyd, hydrolyzed γ-glycidoxypropyltrimethoxysilane. Primer prepared by mixing 2.2 g of a 10% solution of the silane in 1% aqueous acetic acid with 100 g of methanol
[13]A five minute mix time was used

Table 6

BOND STRENGTHS OF 2,6-DIETHYL-*p*-PHENYLENE DIISOCYANATE-TERMINATED 725 MOLECULAR WEIGHT POLYOXYTETRAMETHYLENE GLYCOL-BASED ADHESIVES[1]

SAMPLE NO.	PERCENT ADDITIVE[2]	PRIMER	ALUMINUM SURFACE TREATMENT			TENSILE SHEAR STRENGTH, psi			T-PEEL STRENGTH, piw[6]		
			ALKALI[3]	ACID[4]	$FeSO_4$[5]	-196°C	23°C	150°C	-196°C	23°C	150°C
96640	0.5	A-1120[7]	--	XX	--	3370	4900	1170	17	33	14
96641	0.5	A-1120	--	XX	--	5380	4900	1380	13	33	12
96646	0.25	Hyd[8]	--	XX	--	2000	5100	850	7	15	7
96642	0.5	Hyd	--	XX	--	5400	4500	1460	18	32	18
103801	0.5	Hyd	--	XX	--	3450	4900	1030	11	35	17
96647	0.75	Hyd	--	XX	--	2430	5330	1060	10	25	11
103813	0.7	Hyd	--	XX	--	1900	4670	810	8	30	3
103812[9]	0.7	Hyd	--	XX	--	4400	4620	1300	15	32	16
96644	0.75	--	--	XX	--	3870	4700	1320	16	31	15
96649	0.5	Hyd	XX	XX	XX	MF[10]	4700	1540	30	38	15
103803	0.5	Hyd	XX	XX	--	4970	5050	1200	20	34	21

[1]Adhesives were MOCA-cured (NCO:NH_2 of 1.05). Cure was done at 110°C for 24 hours. Glycol was prepared by mixing glycols of 620 and 1000 molecular weight

[2]Additive was γ-glycidoxypropyltrimethoxysilane, either Z-6040 (Dow Chemical Co.) or A-187 (Union Carbide Co.)

[3]Aluminum was alkaline detergent cleaned at 70°C for 10 minutes in a bath composed of 33.6 g sodium hydroxide, 56.3 g sodium pyrophosphate and 67.2 g sodium metasilicate in 2850 ml water. Panels were rinsed in tap water followed by deionized water. XX indicates use of this treatme

[4]Aluminum was etched at 70°C for 10 minutes in a bath composed of 10 parts sodium dichromate dihydrate and 100 parts concentrated sulfuric acid in 300 parts water. Panels were rinsed in tap water followed by deionized water. XX indicates use of this treatment

[5]Aluminum was removed from the chromic acid bath and immersed for 30 seconds in a 0.1N ferrous sulfate bath at room temperature. Panels were rinsed in tap water followed by deionized water XX indicates use of this treatment

[6]T-peel strengths determined on 0.025" aluminum

[7]A-1120, a 1.0% ethanolic solution (0.02% water) of N-(trimethoxysilylpropyl)ethylenediamine

[8]Hyd, hydrolyzed γ-glycidoxypropyltrimethoxysilane. Primer prepared by mixing 2.2 g of a 10% solution of the silane in 1% aqueous acetic acid with 100 g of methanol

[9]Prepolymer for this experiment was stored separate from the main lot for two weeks prior to us

[10]MF, metal failure at pin hole grip

Table 7

BOND STRENGTHS OF 2,6-DIETHYL-*p*-PHENYLENE DIISOCYANATE-TERMINATED 810 AND 1000 MOLECULAR WEIGHT POLYOXYTETRAMETHYLENE GLYCOL-BASED ADHESIVES[1]

SAMPLE NO.	PREPOLYMER COMPOSITION		PERCENT A-187[2]	PRIMER	CURE CONDITIONS		TENSILE SHEAR STRENGTH, psi			T-PEEL STRENGTH, piw[3]		
	GLYCOL	% NCO			TEMP., °C	TIME, hr	-196°C	23°C	150°C	-196°C	23°C	150°C
96597	PM 810[4]	6.49	0.5	A-1120[5]	110	24	3510	4530	850	14	37	13
96603	PM 810	6.49	1.0	A-1120	110	24	2870	4100	610	9	31	5
96602	PM 810	6.49	1.0	--	110	24	3250	3900	690	12	37	6
81586	PM 1010[6]	5.83	0.5	A-1120	75	72	5850	4130	1030	(13)	(32)	(16)
81647	PM 1010	5.83	0.5	A-1120	75	120	2790	2830	285	(2)	(25)	(1)
90805	PM 1010	6.77	1.0	A-1120	110	24	3870	4230	1010	(13)	(30)	(15)
90849	PM 1010	5.53	0.5	A-1120	110	24	5630	3600	1280	(14)	(44)	(12)
90850	PM 1000[7]	5.78	0.5	A-1120	110	24	4650	3790	1410	(12)	(39)	(9)
96567	PM 1000	5.72	0.5	A-1120	110	24	4540	3690	800	12(14)	59(59)	12(13)
96556	PM 1010	5.53	1.0	Stafoam[8]	110	24	4660	3510	1110	(8)	(7)	(3)
96580A	PM 1000	5.72	0.5	0.1% A-1120, dp[9]	110	24			880			19
B	PM 1000	5.72	0.5	0.05% A-1120, dp	110	24			910			16
C	PM 1000	5.72	0.5	0.01% A-1120, dp	110	24			860			19
96585A	PM 1000	5.72	0.5	0.1% A-1120, dp	110	24			920			16
B	PM 1000	5.72	0.5	0.05% a-1120, dp	110	24			930			20
C	PM 1000	5.72	0.5	0.01% A-1120, dp	110	24			870			19
96586A[10]	PM 1000	5.72	0.5	0.1% A-1120, dp	110	24			970			20
B	PM 1000	5.72	0.5	0.05% A-1120, dp	110	24			970			18
C	PM 1000	5.72	0.5	0.01% A-1120, dp	110	24			870			19

[1]Adhesives were MOCA-cured (NCO:NH_2 of 1.05). Aluminum was etched in standard sulfuric acid-sodium dichromate bath at 70°C for ten minutes

[2]A-187, γ-glycidoxypropyltrimethoxysilane

[3]T-peel strengths determined on 0.025" aluminum except for those in parenthesis which were determined on 0.032" aluminum

[4]PM 810, Polymeg 810, glycol prepared by mixing 620 and 1000 molecular weight polyoxytetramethylene glycol

[5]A-1120, a 1.0% ethanolic solution of N-(trimethoxysilylpropyl)ethylenediamine

[6]PM 1010, Polymeg 1010, Quaker Oats Co. (1010 molecular weight polyoxytetramethylene glycol)

[7]PM 1000, Polymeg 1000, Quaker Oats Co. (1000 molecular weight polyoxytetramethylene glycol)

[8]Stafoam, 25% methyl ethyl ketone solution of Stafoam AA-1802 containing 1.0% A-187, applied with nylon paint brush. Primer dried four hours at room temperature prior to applying adhesive

[9]Aluminum primed by dipping into ethanolic solution of A-1120 [N-(trimethoxysilylpropyl)ethylenediamine], allowing the excess to drain off.

[10]Aluminum treated at 100°C for 10 minutes in a bath consisting of 90 ml of 85% phosphoric acid and 51 g of chromium trioxide in 2590 ml water prior to standard chromic acid etch

prepared, a characteristic most likely due to reaction with moisture. It is possible that the presence of these high molecular weight segments enhanced the -196°C T-peel strength. However, the presence of high molecular weight prepolymer segments would also decrease the amount of MOCA required for cure. Since no allowance was made for this in the adhesive preparation, the adhesive was undoubtedly prepared with an excess of MOCA as compared to the amount normally used (*i.e.*, 95% of stoichiometry). Some experiments were carried out to establish the influence, if any, of each of these variables.

It is known that the tear strength of MOCA-cured Adiprene L-100 is significantly influenced by both the cure time and the amount of MOCA used for cure (Ref. 5). Tear strength increases with both cure time and MOCA concentration. Assuming that the -196°C T-peel strength reflected the tear strength of the polymer, a brief study was made to evaluate the influence of both variables on the adhesive strengths, particularly -196°C T-peel strength, of MOCA-cured 2,6-diethyl-*p*-phenylene diisocyanate-terminated polyoxytetramethylene glycols. The data obtained are given in Table 8, Samples 96595, 96622, 96582 and 96583. It is readily apparent that increased MOCA concentration lowers -196°C and +150°C T-peel strengths (compare the above samples with Sample 96596).

Two adhesives were prepared which contained some high molecular weight prepolymer segments. These were made by first capping one mole of 2,4-tolylene diisocyanate with two moles of 620 molecular weight polyoxytetramethylene glycol to give a glycol which in turn was capped with 2,6-diethyl-*p*-phenylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol. The data for the MOCA-cured adhesives are given in Table 9 (Samples 96592, 96562 and 96563). Neither the -196°C nor +150°C strengths were encouraging.

f. Effect of Fillers. At one stage of the development of the 2,6-diethyl-*p*-phenylene diisocyanate-based adhesives discussed in the previous sections, considerable difficulty was encountered in obtaining adequate -196°C T-peel strengths. Since this strength reflects the cohesive strength of the polymer at this temperature, methods for increasing cohesive strength were sought. One approach was the use of fillers, since fiber glass fillers had been reported to significantly increase the -196°C T-peel strength of polyurethane adhesives (Ref. 6). The major part of this study was done using 2,4-tolylene diisocyanate-based adhesives and is discussed in Section A.8. The results obtained using 2,6-diethyl-*p*-phenylene diisocyanate-based adhesives are discussed below and the data are presented in Table 10. Both nylon and glass fibers were used.

The effect of two of the better fiber glass fillers (as found in the study discussed in Section A.8 on the strengths of a 2,6-diethyl-*p*-phenylene diisocyanate-based adhesive was determined (Samples 90824

Table 8

BOND STRENGTHS OF 2,6-DIETHYL-p-PHENYLENE DIISOCYANATE-BASED ADHESIVES PREPARED FROM 1:1 WEIGHT RATIO OF POLYMEG 620 AND POLYMEG 1000-BASED PREPOLYMERS[1]

SAMPLE NO.	PREPOLYMER COMPOSITION: PM 620 % NCO[2]	PM 1000 % NCO[3]	PERCENT A-187[4]	MOCA CONC[5]	CURE CONDITIONS: TEMP., °C	TIME, hr	TENSILE SHEAR STRENGTH, psi: -196°C	23°C	150°C	T-PEEL STRENGTH, piw[6]: -196°C	23°C	150°C
81632	7.04	5.83	0.5	95%	75	72		3880	820		(32)	(7)
90808	8.07	6.77	1.0	95%	110	24	MF[7]	4370	1600	(49)	(23)	(19)
90817	8.07	5.83	1.0	95%	110	24	MF	5300	1640	(44)	(45)	(38)
90839	8.07	5.53	1.0	95%	110	24	4660	4500	1570	(17)	(27)	(16)
90840	7.46	5.53	1.0	95%	110	24	MF	3630	1200	(19)	(58)	(17)
90841	7.46	5.53	0.5	95%	110	24	MF	4730	1470	(23)	(34)	(20)
96559	7.46	5.78	1.0	95%	110	24	5410	4630	1120	(13)	(25)	(14)
96560[8]	7.46	5.53	0.5	95%	110	24	3450	4650	970	(16)	(26)	(12)
96570	7.83	5.72	0.5	95%	110	24	MF	4360	1330	47(55)	30(28)	16(19)
96589	7.83	5.72	0.5	95%	110	24	4480	2190	1090	43	32	12
96591	7.83	5.72	0.5	95%	110	24	2000	4170	620	9	36	8
96596	7.83	5.72	0.5	95%	110	24	3470	4950	960	12	37	13
96621	8.09	5.53	0.5	95%	110	24	2410	4490	720	8	41	4
96631	8.09	5.53	0.5	95%	110	24	1470	3300	400	13	19	2
96595	7.83	5.72	0.5	100%	110	24	1430	3610	380	3	21	2
96622	8.09	5.53	0.5	100%	110	72	1620	3770	550	6	28	2
96582	7.83	5.72	0.5	105%	110	24	2300	3720	700	2	27	2
96583	7.83	5.72	0.5	105%	110	72	2270	3870	790	4	27	3
90844[9]	7.46	5.53	0.5	95%	110	24	MF	4570	920	(33)	(27)	(17)
96561[8,10]	7.46	5.53	1.0	95%	110	24	4340	3970	1000	(11)	(23)	(15)
90845[11]	7.46	5.53	0.5	95%	110	24	MF	4600	933	(13)	(19)	(15)

[1]Adhesives were MOCA-cured. Aluminum was etched in standard sulfuric acid-sodium dichromate bath at 70°C for ten minutes. Aluminum primed with 1.0% ethanolic solution of N-(trimethoxysilylpropyl)-ethylenediamine except for Samples 90844 and 96561

[2]PM 620, Polymeg 620, Quaker Oats Co. (620 molecular weight polyoxytetramethylene glycol)

[3]PM 1000, Polymeg 1000, Quaker Oats Co. (1000 molecular weight polyoxytetramethylene glycol)

[4]A-187, γ-glycidoxypropyltrimethoxysilane

[5]Percent of stoichiometric amount

[6]T-peel strengths determined on 0.025" aluminum except for those in parenthesis which were determined on 0.032" aluminum

[7]MF, metal failure at pin hole grip

[8]Panels were placed in dry nitrogen atmosphere after priming and until adhesive was applied

[9]Primer was hydrolyzed γ-glycidoxypropyltrimethoxysilane. Primer prepared by mixing 2.2 g of a 10% solution of the silane in 1% aqueous acetic acid with 100 g of methanol

[10]No primer used

[11]This adhesive was cured with MOCA used as received

Table 9

BOND STRENGTHS OF 2,6-DIETHYL-*p*-PHENYLENE DIISOCYANATE-BASED ADHESIVES PREPARED FROM MISCELLANEOUS GLYCOL-BASED PREPOLYMER[1]

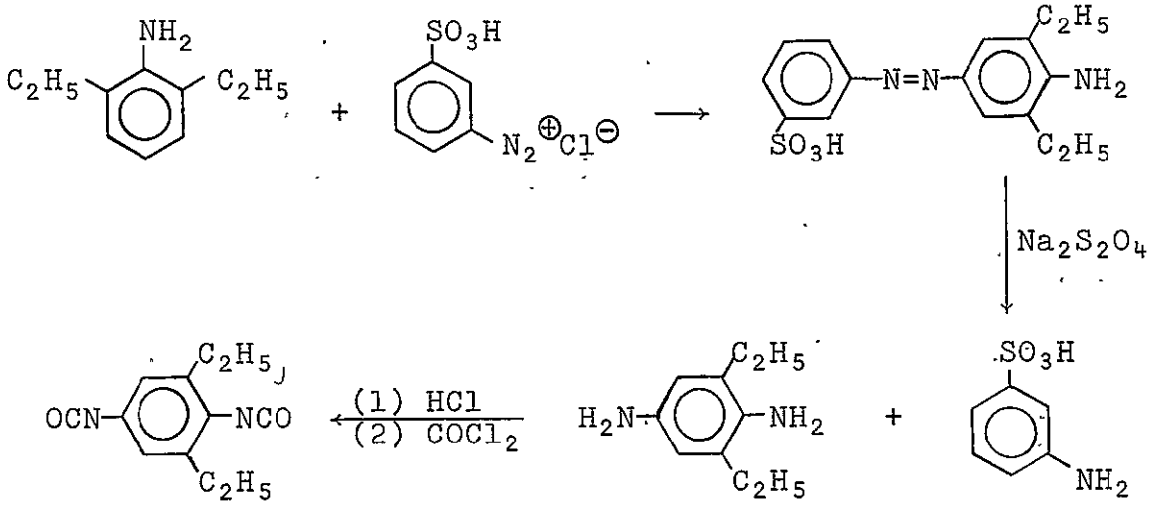
SAMPLE NO.	PREPOLYMER COMPOSITION		PREPOLYMER WT. RATIO	PERCENT A-187[2]	CURE CONDITIONS		TENSILE SHEAR STRENGTH, psi			T-PEEL STRENGTH, piw[3]		
	GLYCOL	% NCO			TEMP., °C	TIME, hr	-196°C	23°C	150°C	-196°C	23°C	150°C
90847	PM 620[4] PM 1010[5]	7.46 5.53	4:1	0.5	110	24	MF[6]	MF	1200	(18)	(26)	(17)
90846	PM 620 PM 1010	7.46 5.53	3:2	0.5	110	24	MF	5100	1110	(23)	(29)	(15)
96576	PM 620 PM 1000[7]	7.83 5.72	2:3	0.5	110	24	4600	4830	970	14	37	16
96579	PM 620 PM 1000	7.83 5.72	1:4	0.5	110	24	1820	3030	370	4	29	2
96592[8]	PM 620 PM 620-T[9]	7.83 4.44	95:5	0.5	110	24	3130	4750	1000	13	28	14
96562	PM 620 PM 620-T	7.46 4.44	85:15	0.5	110	24	3770	5150	1190	(18)	(29)	(17)
96563	PM 620 PM 620-T	7.46 4.44	75:25	0.5	110	24	2560	4990	910	(11)	(33)	(9)
81650	PM 620 PM 620-TC[10]	7.04 8.31	75:25	0.5	75	120	4660	4630	1495	(12)	(91)	(51)

[1]Adhesives were MOCA-cured ($NCO:NH_2$ of 1.05). Aluminum was etched in standard sulfuric acid-sodium dichromate bath at 70°C for ten minutes. Aluminum primed with 1.0% ethanolic solution of N-(trimethoxysilylpropyl)ethylenediamine.
[2]A-187, γ-glycidoxypropyltrimethoxysilane
[3]T-peel strengths determined on 0.025" aluminum except for those in parenthesis which were determined on 0.032" aluminum
[4]PM 620 Polymeg 620, Quaker Oats Co. (620 molecular weight polyoxytetramethylene glycol)
[5]PM 1010, Polymeg 1010, Quaker Oats Co. (1010 molecular weight polyoxytetramethylene glycol)
[6]MF, metal failure at pin hole grip
[7]PM 1000, Polymeg 1000, Quaker Oats Co. (1000 molecular weight polyoxytetramethylene glycol)
[8]$NCO:NH_2$ of 1.00 used
[9]PM 620-T, 2,4-tolylene diisocyanate capped with 620 molecular weight polyoxytetramethylene glycol
[10]PM 620-TC, 2,4-tolylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol

and 90828). Tensile shear strengths were not significantly affected (by using 20 weight percent filler) but the desired increase in -196°C T-peel strength was not obtained.

One nylon fiber and one glass fiber were also tested as fillers at approximately five volume percent. Samples 96557, 06578 and 96569 give the results obtained. Again, neither fiber offered any advantage in adhesive strengths and both decreased the pot life.

g. Diisocyanate Synthesis. During the course of this project, about 2200 g of 2,6-diethyl-*p*-phenylene diisocyanate were prepared for use in adhesive studies. Most of this compound was prepared via the route shown below.



The details of this procedure are given in the Experimental Section and are modifications of the procedure of Case (Ref. 7). This procedure requires the use of a 12-liter reaction flask to obtain approximately 140 g of the intermediate diamine dihydrochloride. A considerable amount of work is involved, therefore, in preparing significant quantities of the diisocyanate.

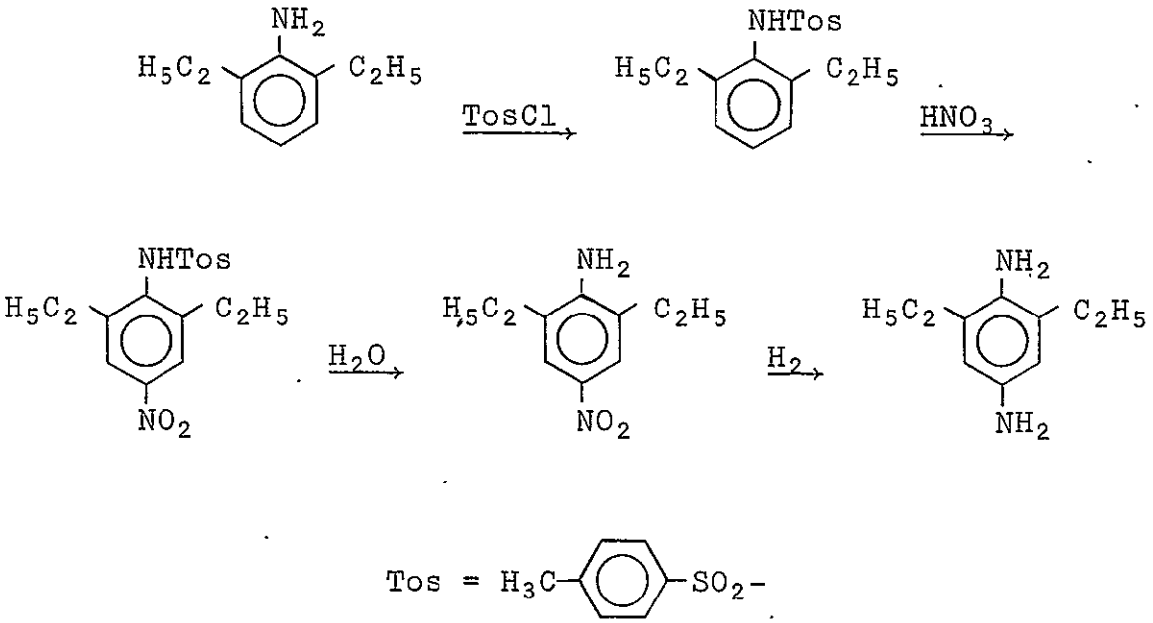
An alternate method was investigated (Refs. 8 and 9) which potentially would have permitted more diamine to be prepared in less time even though the number of steps was larger. The synthetic route is shown below.

Table 10

EFFECT OF SELECTED FILLERS ON BOND STRENGTHS
OF 2,6-DIETHYL-*p*-PHENYLENE DIISOCYANATE-BASED ADHESIVES[1]

SAMPLE NO.	PREPOLYMER COMPOSITION		PERCENT A-187[2]	FILLER	FILLER WT. %	TENSILE SHEAR STRENGTH, psi			T-PEEL STRENGTH, piw[3]		
	GLYCOL	% NCO				-196°C	23°C	150°C	-196°C	23°C	150°C
90800	PM 620[4]	8.07	1.0	--	--	MF[5]	5350	1910	16	32	39
90824	PM 620	8.07	1.0	A-1120 sized 709 glass fibers[6]	30	MF	5170	1910	16	24	11
90828	PM 620	8.07	1.0	A-1120 sized 709 glass fibers[7]	20	5230	5400	1760	7	24	12
96569	PM 620	7.83	0.5	709 glass fibers	11	4440	MF	1440	(14)	(27)	(12)
96578[8]	PM 620	7.83	0.5	nylon fibers[9]	5	4420	5670	1290	(9)	(50)	(47)
96557	PM 620	7.46	0.5	nylon fibers	5	3780	5090	1750	6	76	45

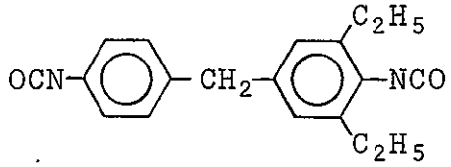
[1]Adhesives were MOCA-cured. Cure was 110°C for 24 hours
[2]A-187, γ-glycidoxypropyltrimethoxysilane
[3]T-peel strengths determined on 0.032" aluminum except for values in parenthesis which were obtained on 0.025" aluminum
[4]PM 620, Polymeg 620, Quaker Oats Co. (620 molecular weight polyoxytetramethylene glycol)
[5]MF, metal failure at pin hole grip
[6]Glass fibers (Owens Corning Glass Co.) sized with N-(trimethoxysilylpropyl)ethylene diamine
[7]Glass fibers (Owens Corning Glass Co.) sized with γ-glycidoxypropyltrimethoxysilane
[8]Nylon fibers dried at 70°C and 1 mm
[9]Nylon fibers supplied by Dr. W. E. Hill, NASA, Huntsville, Alabama



Tos = H_3C–C$_6$H$_4$–SO_2–

This reaction worked well on a small scale. However, when attempted on a 12-liter scale the nitration step gave very poor yields. The diamine was, therefore, prepared by the former method, so that further adhesive development would not be delayed.

2. 3,5-Diethyl-4,4'-Diisocyanatodiphenylmethane-Based Adhesives. Polyurethane adhesives based on 2,6-diethyl-*p*-phenylene diisocyanate can be prepared which fulfill the contract goals as was discussed in the previous section. A shortcoming of this diisocyanate which could potentially make its use undesirable is the possible carcinogenic character of the diamine intermediate. Many *p*-phenylenediamines have been shown to be carcinogens. For this reason some attention was given to adhesives based on 3,5-diethyl-4,4'-diisocyanato diphenylmethane,



The intermediate diamine, in this case, represents a family of diamines known to considerably less carcinogenic than the *p*-phenylenediamines.

This particular diisocyanate was desirable for two reasons. First, it had already been shown that an aromatic isocyanate function hindered by two ortho ethyl groups had a reaction rate with MOCA which was slow enough to give desirable pot lives. Second, the linear

configuration of the two isocyanate functions was expected to result in the best adhesive strengths at elevated temperatures as found with 2,6-diethyl-*p*-phenylene diisocyanate.

Following the procedure of Case (Ref. 7) 3,5-diethyl-4,4'-diisocyanatodiphenylmethane was prepared. Details are given in the Experimental Section.

Two prepolymers were prepared by capping 1000 molecular weight polyoxytetramethylene glycols, one having an NCO content less than theoretical. As was the case with the 2,6-diethyl-*p*-phenylene diisocyanate-based adhesives, the prepolymer with uncombined diisocyanate had a poor shelf life. A precipitate formed after a few weeks.

The initial adhesive strengths were encouraging (Sample 90822 of Table 11). Only 150°C tensile shear strengths and -196°C T-peel strengths were checked, as these two strength goals are usually the most difficult to obtain simultaneously. A cure time of 48 hours at 110°C appeared to be adequate. The pot life was estimated (viscosity versus time measurements) to be about two hours. A subsequent test of this adhesive at all three test temperatures gave less impressive results (Sample 90829). However, this formulation contained only 0.5% additive. The surprising result was the very low -196°C T-peel strength as compared to the initial results.

Better adhesive strengths were obtained using the second prepolymer, i.e., the one with excess diisocyanate. Samples 96623, 103,802, 103,814 and 103,815 give the results obtained with and without primer and using two surface treatments.

Sample 103,802 was an attempt to repeat Sample 96623. There was a period of 19 days between these preparations. Both -196°C and +150°C strengths decreased as was found for the 2,6-diethyl-*p*-phenylene diisocyanate-based adhesives.

Using the alkali-chromic acid-ferrous sulfate surface treatment result in increased strengths (Sample 103,814). Only the 150°C tensile shear strength was below target values. This may be near the optimum 150°C tensile shear strength, since the mode of failure was estimated to be about 70% cohesive. However, some improvement in bulk strength of this polymer might be expected by using fresh prepolymers, *i.e.*, prepolymers that had not been exposed to air.

Using no primer (Sample 103,815) resulted in a decrease in both tensile shear and T-peel strengths.

Table 11

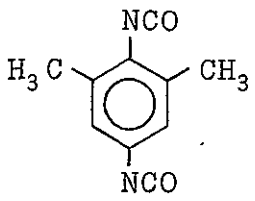
BOND STRENGTHS OF

3,5-DIETHYL-4,4'-DIISOCYANATODIPHENYLMETHANE-BASED ADHESIVES[1]

SAMPLE NO.	PREPOLYMER COMPOSITION		PERCENT A-187[2]	PRIMER	CURE CONDITIONS		TENSILE SHEAR STRENGTH, psi			T-PEEL STRENGTH, piw		
	GLYCOL	% NCO			TEMP., °C	TIME, hr	-196°C	23°C	150°C	-196°C	23°C	150°C
90822A[3]	PM 1010[4]	5.12	1.0	A-1120[5]	110	24			1390	48		
B[3]	PM 1010	5.12	1.0		110	48			1280	63		
C[3]	PM 1010	5.12	1.0		110	72			1310	64		
90829[3]	PM 1010	5.12	0.5	A-1120	110	24	2370	3570	865	11	90	12
96623[3]	PM 1000[6]	5.52	0.5	Hyd[7]	110	24	5230	3330	1230	26	63	25
103802[3]	PM 1000	5.52	0.5	Hyd	110	24	4350	3700	1080	10	80	17
103814[8]	PM 1000	5.52	0.5	Hyd	110	24	MF[9]	3700	1280	40	69	23
103815[8]	PM 1000	5.52	0.75	--	110	24	3250	3820	720	15	93	15

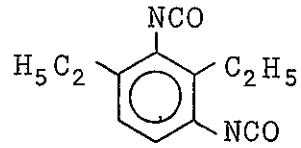
[1]Adhesives were MOCA cured
[2]A-187, γ-glycidoxypropyltrimethoxysilane
[3]Aluminum etched in standard sulfuric acid-sodium dichromate bath at 70°C for 10 minutes
[4]PM 1010, Polymeg 1010, Quaker Oats Co. (1010 molecular weight polyoxytetramethylene glycol)
[5]A-1120, N-(trimethoxysilylpropyl)ethylenediamine
[6]PM 1000, Polymeg 1000, Quaker Oats Co. (1000 molecular weight polyoxytetramethylene glycol)
[7]Hyd, hydrolyzed γ-glycidoxypropyltrimethoxysilane (A-187). Primer prepared by mixing 2.2 g of a 10% solution of A-187 in 1% aqueous acetic acid with 100 g of methanol
[8]Aluminum was etched in an alkali bath, then in chromic acid and rinsed in ferrous sulfate. Details in Experimental Section
[9]MF, metal failure at pin hole grip

3. Adhesives Based on Other New Diisocyanates. Ten new diisocyanate structures other than the two already discussed were investigated for their effect on reactivity and bond strength of the corresponding adhesives. Each of these diisocyanates will be discussed along with the reason for their elimination as potential candidates. The structures of these diisocyanates are given below:



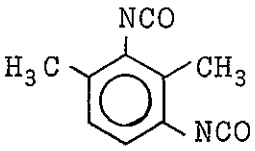
I

2,6-dimethyl-*p*-phenylene diisocyanate



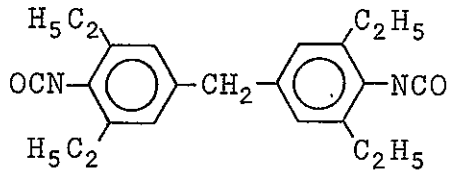
II

2,4-diethyl-*m*-phenylene diisocyanate



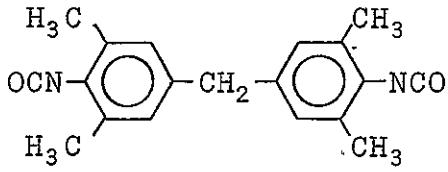
III

2,4-dimethyl-*m*-phenylene diisocyanate



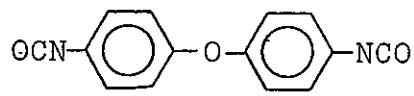
IV

3,3',5,5'-tetraethyl-4,4'-diisocyanatodiphenylmethane



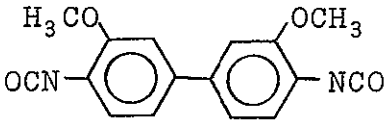
V

3,3',5,5'-tetramethyl-4,4'-diisocyanatodiphenylmethane



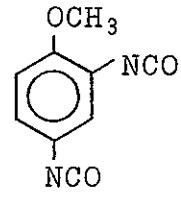
VI

4,4'-diisocyanatodiphenyl ether



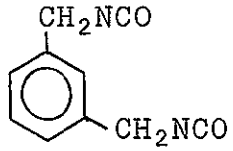
VII

3,3'-dimethoxy-4,4'-biphenylene diisocyanate



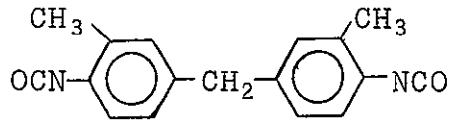
VIII

4-methoxy-*m*-phenylene diisocyanate



IX

m-xylylene
diisocyanate



X

3,3'-dimethyl-4,4'-
diisocyanatodiphenylmethane

All of the above diisocyanates except 3,3'-dimethoxy-4,4'-biphenylene diisocyanate and 3,3'-dimethyl-4,4'-diisocyanatodiphenylmethane were synthesized from the corresponding diamines by reaction with phosgene. The generalized procedure used is given in the Experimental Section. Purification of commercial products gave 3,3'-dimethoxy-4,4'-biphenylene diisocyanate and 3,3'-dimethyl-4,4'-diisocyanatodiphenylmethane. The data concerning bond strengths and reactivities are given in Table 12.

The investigation of 2,6-dimethyl-*p*-phenylene diisocyanate (I) was begun at the same time as the study of 2,6-diethyl-*p*-phenylene diisocyanate. It was thought that the dimethyl-substituted diisocyanate would have improved elevated temperature properties as compared with the diethyl analogue, because it contains a smaller side chain. A prepolymer based on a 1020 molecular weight polyoxytetramethylene glycol was prepared. This 1020 molecular weight glycol was used in preference to the 620 molecular weight glycol, since it was known from the work of Case (Ref. 7) that the dimethyl analogue reacted about twice as fast as the diethyl.

A 2,6-dimethyl-*p*-phenylene diisocyanate-based adhesive was prepared. This adhesive (Sample 81599 of Table 12) had a very high Vicat softening temperature, 214°C, showing the benefit obtained from the para configuration of the isocyanate groups. The 150°C adhesive strengths of this adhesive were surprisingly low, however. The tensile shear specimens tested at 150°C exhibited only adhesive failure. The T-peel specimens gave total cohesive failure at all three temperatures. This data indicate that the polymer had good tensile strength but poor tear strength, probably due to under cure. The pot life of the above adhesive, Sample 81599, was estimated to be about 145 minutes based on viscosity versus time measurements. Increasing the cure temperature to 90°C surprisingly did not result in increased strengths (Sample 90771). Similarly, addition of an epoxy additive also did not result in any benefit in adhesive strengths (Sample 81609).

As discussed earlier, the type of failure occurring during T-peel tests of the 2,6-diethyl-*p*-phenylene diisocyanate-based adhesives during early stages of development was generally cohesive, even at

room temperature. Since these polymers were quite rigid, as indicated by Vicat softening data, it was thought possible that the low T-peel strengths were the result of a high degree of chain packing. Possibly there were not enough amorphous regions in the polymer to give the required ductility. To test this hypothesis a highly hindered diisocyanate structurally related to 2,4-tolylene diisocyanate was prepared. This diisocyanate was 2,4-diethyl-*m*-phenylene diisocyanate (II).

Two MOCA-cured 2,4-diethyl-*m*-phenylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol adhesives were prepared. One was cured at 75°C and the other at 90°C, both for 72 hours. The results are shown in Table 12 (Samples 90758 and 90761). The tensile shear and T-peel strengths of this type of adhesive were low, even when a 90°C cure was used. However, only cohesive failure was observed in the T-peel specimens again, indicating possible inadequate cure.

The pot life of the above adhesive was very short, about 35 minutes. The reason for this is not known. However, there is some evidence that a urethane group meta to an isocyanate group increases the reaction rate of the isocyanate function relative to a para urethane group (Ref. 10). This, coupled with the higher initial viscosity of the prepolymer prepared from the meta diisocyanate, probably accounts for the relatively short pot life.

Adhesives based on 2,4-dimethyl-*m*-phenylene diisocyanate (III) were also prepared and tested (Samples 90759 and 90765 of Table 12). Both the tensile shear and T-peel strengths at -196°C and 150°C were below target values. Except for the -196°C T-peel specimens, only adhesive failure was observed, indicating that increased strengths are possible. As before, the adhesive prepared from the meta diisocyanate reacted much faster than the para diisocyanate-based adhesive. The high Vicat softening temperature indicated a very high modulus polymer.

An adhesive was prepared from a 3,3',5,5'-tetraethyl-4,4'-diisocyanatodiphenylmethane(IV)-terminated 620 molecular weight polyoxytetramethylene glycol prepolymer. Although a very high Vicat softening temperature was obtained, 201°C, the tensile shear and T-peel strengths were below the target values both at -196°C and +150°C, (Sample 81595).

Cohesive failure was found in the T-peel specimens at all three test temperatures indicating poor tear strength, again possibly due to inadequate cure. In addition the pot life was only about 20 minutes due mainly to the high initial viscosity.

No attempt was made to prepare an adhesive of 3,3',5,5'-tetramethyl-4,4'-diisocyanatodiphenylmethane (V) due to its high melting point (131°C). A prepolymer prepared from this diisocyanate would probably be very viscous, and the corresponding adhesive would, therefore, have a short pot life.

When 4,4'-diisocyanatodiphenyl ether (VI) was used in a 620 molecular weight polyoxytetramethylene glycol-based adhesive, the polymer gelled in less than three minutes during mixing.

The presence of a methoxy group ortho to an isocyanate function is known to decrease the isocyanate-amine reaction rate (Ref. 11). Two adhesives were prepared utilizing prepolymers based on the methoxy-hindered diisocyanates, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate (VII), and 4-methoxy-*m*-phenylene diisocyanate (VIII), to determine the effect of these structures on adhesive properties. Both adhesives, Samples 71420 and 71421, had poor 150°C strengths. Further cure at 150°C (24 hours) did not improve the 150°C tensile shear strengths of either adhesive. This indicates that full cure was obtained and that the low 150°C strengths are characteristics of the polymer.

The initial preparation of a *m*-xylylene diisocyanate(IX)-based adhesive showed that adequate strengths could be obtained except for the 150°C tensile shear strength (Sample 71418). However, the pot life of this adhesive was very short, much shorter than had been expected. The rapid cure was later shown to be related, at least in part, to the amount of hydrolyzable chlorides present. A study of the effect of hydrolyzable chloride concentration on reaction rate is discussed later in this report.

Redistillation of the *m*-xylylene diisocyanate lowered the percent hydrolyzable chlorides by about 75%. This resulted in a three-fold increase in pot life of the corresponding adhesive (Sample 71437). The 150°C tensile shear strength also increased. Still further purification of *m*-xylylene diisocyanate was carried out. The pot life of the corresponding adhesive did not improve significantly. In addition, the adhesive strengths were not sufficiently high to warrant further consideration of this diisocyanate (Sample 81576 of Table 12).

A prepolymer was prepared from 3,3'-dimethyl-4,4'-diisocyanatodiphenylmethane (X), with a 1000 molecular weight polyoxytetramethylene glycol. Samples 90775A, B and C (Table 12) give the corresponding adhesive data when a MOCA cure was employed. Adhesives based on this diisocyanate require higher cure temperatures than the corresponding 2,4-tolylene diisocyanate-based adhesives.

The 150°C tensile shear and T-peel strengths were not as good as those obtained with the 2,4-tolylene diisocyanate based adhesive and in addition, the pot life was only about 30 minutes due mainly to a high initial viscosity. The corresponding 2,4-tolylene diisocyanate adhesive has a pot life of 44 minutes.

Aliphatic isocyanates are known to react slower than aromatic isocyanates. However, polymers based on aliphatic diisocyanates are more flexible than the corresponding aromatic diisocyanate-based polymers and do not have sufficient strength at elevated temperatures to be usable in the application under study. In an attempt to utilize the low reactivity of hexamethylene diisocyanate and still retain elevated temperature strengths, a low molecular weight prepolymer was prepared with a 381 molecular weight polyoxytetramethylene glycol. The prepolymer was a solid but could be processed in the molten state at 40°C. The adhesive strengths obtained are shown in Table 12 (Sample 71419).

It is obvious that the desired elevated temperature properties are not present, but the pot life was adequate. These results, along with those obtained with two other aliphatic isocyanate-based adhesives tested previously (Ref. 4), indicate that this type of adhesive also lacks adequate low temperature strength. The hexamethylene diisocyanate and 4,4'-methylenebis(cyclohexyl isocyanate)-capped 620 molecular weight polyoxytetramethylene glycol-based adhesives had -196°C tensile shear strengths of 2867 and 1917 psi, respectively (target, 4000 psi at -253°C).

The exceedingly fast cures obtained with some of the above diisocyanates indicated the presence of impurities that were catalyzing the reaction. Some of the isocyanates were analyzed for hydrolyzable chlorides using the ASTM 1638-61T test method. The results indicated that pot life was influenced by the hydrolyzable chloride content. The results obtained with *m*-xylylene diisocyanate-based adhesives showed this trend quite clearly.

The effect of acidity on pot life was further investigated employing a MOCA-cured 2,4-tolylene diisocyanate-terminated 1000 molecular weight polyoxytetramethylene glycol. The hydrolyzable chloride content was increased by the addition of benzoyl chloride to the prepolymer. The pot life was taken as the time for the viscosity of the MOCA-cured samples to reach 200,000 cps. A MOCA-cured Adiprene L-100 adhesive, used as a reference point, reaches this viscosity in about 60 minutes. The pot life plotted against percent hydrolyzable chloride is shown in Figure 1. A decrease in pot life occurs as the hydrolyzable chloride content increases. These pot lives are much longer than those found with the *m*-xylylene diisocyanate-based adhesive. Possibly other impurities, such as small quantities of ureas, could be effecting the reaction rate of *m*-xylylene diisocyanate based adhesive.

Table 12

BOND STRENGTHS AND POT LIVES OF POLYURETHANE ADHESIVES BASED ON SYNTHESIZED DIISOCYANATES[1]

SAMPLE NO.	PREPOLYMER COMPOSITION				APPROX. POT LIFE[3]	CURE CONDITIONS		TENSILE SHEAR STRENGTH, psi			T-PEEL STRENGTH, piw			VICAT SOFTENING TEMP., °C
	GLYCOL	ISOCYANATE	% NCO	% HC[2]		TEMP., °C	TIME, hrs	-196°C	23°C	150°C	-196°C	23°C	150°C	
81599	PM 1020[4]	DMPDI[5]	6.21	0.019	145	75	72	4500	4065	700	8	132	3	214
90771	PM 1020	DMPDI	6.21	0.019		90	72	1400	3670	890	2	67	1	
81609[6]	PM 1020	DMPDI	6.21	0.019		75	72	2700	3820	980	2	108	2	
90758	PM 620[7]	DEMDI[8]	7.95		35	75	72	1760	4170	1010	3	7	8	193
90761	PM 620	DEMDI	7.95			90	72	2700	4300	1030	6	14	10	200
90759	PM 1010[9]	DMMDI[10]	6.03		50	75	72	3100	2870	1020	6	11	5	220
90765	PM 1010	DMMDI	6.03			90	72	3100	2770	1120	6	65	6	>227
81595	PM 620	TEMDI[11]	6.14	0.006	20	75	72	860	2720	540	6	4	1	201
71421	PM 620	DADI[12]	6.54		~120	75	24	4800	4400	26		38	8	
71420	PM 620	ADI[13]	8.23	0.0135	~30	75	24	3650	3273	10		38	0	
71418	PM 620	XDI[14]	8.01	0.136	~10	75	24	4370	3020	460		34	35	148
71437	PM 620	XDI	7.85	0.0324	~30	75	24	3400	1990	724	14	21	30	
81576	PM 620	XDI	8.30	0.007	15	75	24	3520	4070	500	9	47	30	
90755A	PM 1010	DMM[15]	4.93		30	75	24			815			1	
B	PM 1010	DMM	4.93			90	24			705			2	
C	PM 1010	DMM	4.93			110	24			910			31	
71419	PM 381[16]	HMDI[17]	11.32		~120	75	24	1710	3540	300		107	15	92

[1]Adhesives were MOCA cured and contained 0.5% γ-glycidoxypropyltrimethoxysilane additive. Aluminum was etched in standard sulfuric acid-sodium dichromate bath at 70°C for ten minutes. After drying the aluminum was primed with 1.0% ethanolic solution of N-(trimethoxysilylpropyl)ethylenediamine

[2]Hydrolyzable chloride as determined on diisocyanate

[3]Pot life determined by technique given in Experimental Section. Approximate values estimated by visual observation of the adhesive mixture

[4]PM 1020, Polymeg 1020, Quaker Oats Co. (1020 molecular weight polyoxytetramethylene glycol)

[5]DMPDI, 2,6-dimethyl-*p*-phenylene diisocyanate

[6]Adhesive contains 1% Epon 828 additive

[7]PM 620, Polymeg 620, Quaker Oats Co. (620 molecular weight polyoxytetramethylene glycol)

[8]DEMDI, 2,4-diethyl-*m*-phenylene diisocyanate

[9]PM 1010, Polymeg 1010, Quaker Oats Co. (1010 molecular weight polyoxytetramethylene glycol)

[10]DMMDI, 2,4-dimethyl-*m*-phenylene diisocyanate

[11]TEMDI, 3,3',5,5'-tetraethyl-4,4'-diisocyanatodiphenylmethane

[12]DADI, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, Upjohn Chemical Co.

[13]ADI, 4-methoxy-*m*-phenylene diisocyanate

[14]XDI, *m*-xylylene diisocyanate

[15]DMM, 3,3'-dimethyl-4,4'-diisocyanatodiphenylmethane, Aldrich Chemical Co.

[16]PM 381, Polymeg 381, Quaker Oats Co., (381 molecular weight polyoxytetramethylene glycol)

[17]HMDI, Mondur HX, Mobay Chemical Co., (hexamethylene diisocyanate)

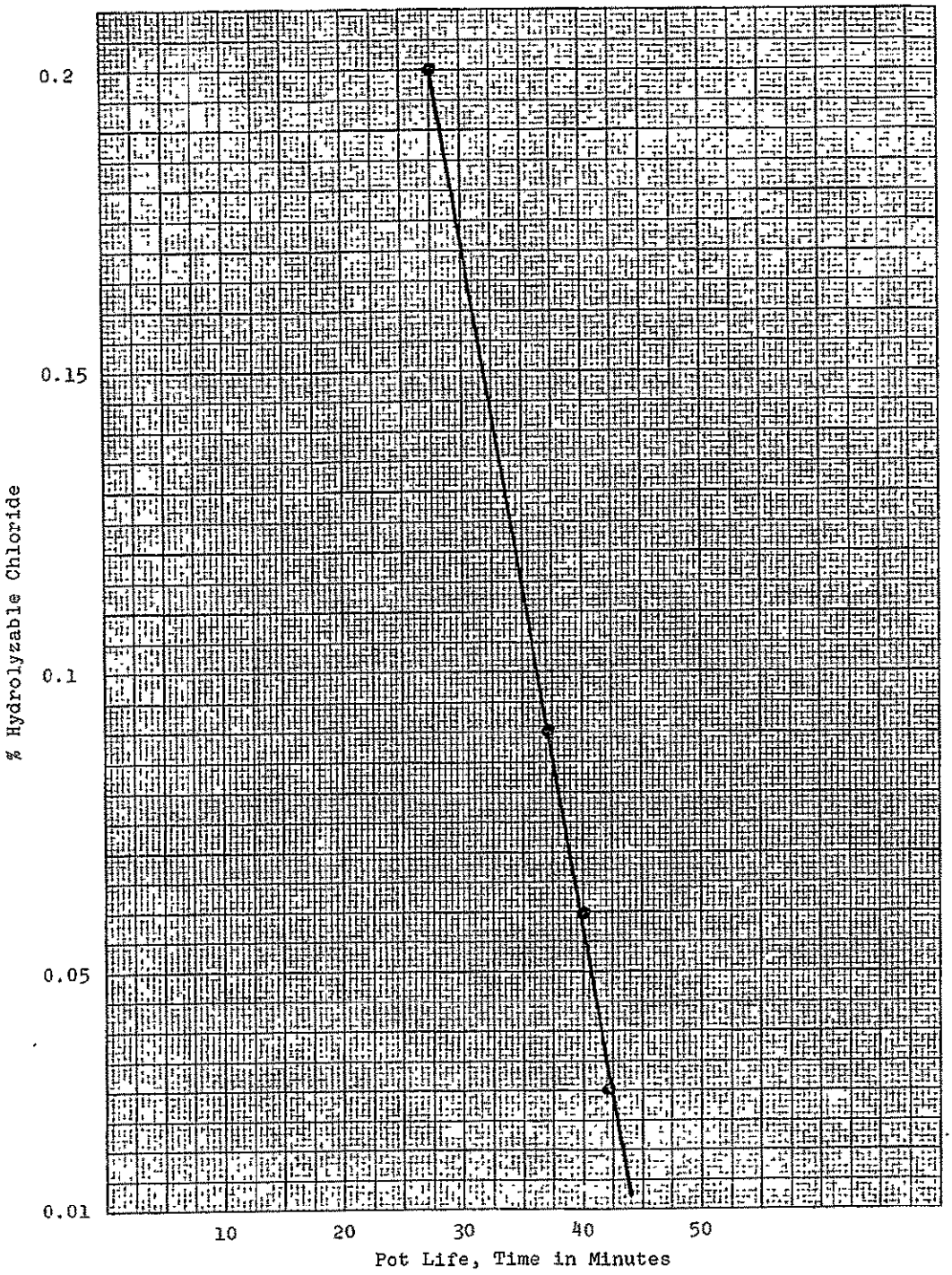


Figure 1. Influence of Hydrolyzable Chloride on Pot Life

4. Effect of Curing Agent Structure. During the first year of this program we showed that the desired adhesive strengths could be approached using MOCA-cured 2,4-tolylene diisocyanate-terminated 620 or 1000 molecular-weight polyoxytetramethylene glycols. The pot lives of these adhesives, 9 and 44 minutes respectively, were considerably shorter than the goal of 120 minutes. Therefore, an investigation was directed toward development of an aromatic diamine curing agent to replace MOCA. The objective was to prepare a diamine with sufficiently less reactivity than MOCA to give the desired pot life while retaining the properties of the MOCA-cured polymer.

A systematic study of the effect of various functional groups on reactivity of 4,4'-methylenebisanilines was carried out.

Outlined in Table 13 are the curing agents considered. The substituent groups were chosen so that the influence of both amine basicity and steric hindrance could be evaluated. Specific substituent groups were selected based on their known abilities to withdraw electrons from the aromatic rings as estimated using the Hammett sigma parameters.

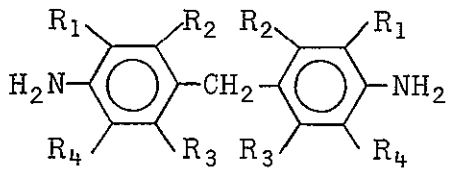
The remarks in Table 13 summarize the results of the work. With respect to pot life and adheisve strengths, curing agent XIV proved to be the best of those compounds to be prepared. Curing agent XVII can be prepared by the aniline-formaldehyde condensation method, but as will be discussed later in this report, the amine was evidently too weak to provide adequate cure at the maximum temperature considered practical. Attempts to prepare curing agents XVI, XIX, XXI, XXII and XXIII under the same conditions used for the preparation of curing agent XVII resulted in no product. Evidently the presence of these various combinations of substituents deactivates the aromatic ring, preventing condensation with formaldehyde. The preparation of curing agent XX was apparently accomplished but purification of the product by several technqiues was unsuccessful.

Four other diamines were tested for their influence on reactivity and adhesive bond strengths. These curing agents were Curalon L (a product of Naugatuck Chemical Company), 4,4'-diaminodiphenylsulfone, 2,6-diaminopyridine and the bis(*p*-aminobenzoate) of triethylene glycol. The bond strength and pot life data obtained with all the above curing agents are given in Table 14. Corresponding MOCA-cured adhesives are included for comparison.

The bromo analogue of MOCA, 4,4'-methylenebis-(2-bromoaniline), m.p. 118°C, was used to cure a 2,4-tolylene diisocyanate-terminated 1000 molecular weight polyoxytetramethylene glycol. It was added to the prepolymer as a liquid to duplicate the method generally used with

Table 13

PROPOSED CURING AGENTS FOR POLYURETHANE ADHESIVES



CURING AGENT	R_1	R_2	R_3	R_4	REMARKS
XI	Cl	H	H	H	MOCA, rapid reaction rate
XII	Br	H	H	H	Cure more rapid than MOCA
XIII	Cl	Cl	H	H	High melting, insoluble
XIV	Cl	H	Cl	H	Soluble, satisfactory reaction rate
XV	Cl	H	H	Cl	High melting, insoluble
XVI	H	Cl	Cl	H	Preparation not successful[1]
XVII	CF_3	H	H	H	Inadequate cure
XVIII	NO_2	H	H	H	High melting, insoluble
XIX	Cl	H	CF_3	H	Preparation not successful[1]
XX	Cl	H	OCH_3	H	Prepared in impure state only
XXI	OCH_3	H	CF_3	H	Preparation not successful[1]
XXII	F	H	CF_3	H	Preparation not successful[1]
XXIII	H	CF_3	CF_3	H	Preparation not successful[1]
XXIV	C_2H_5	H	H	C_2H_5	Gelation in less than one minute

[1]The corresponding aniline would not condense with formaldehyde under the same conditions used to prepare Curing Agent XV

MOCA. Even though a comparable Vicat softening temperature was obtained, the bond strengths of the adhesive were not as good as those obtained with a MOCA cure of the same prepolymer. These data are given in Table 14, Sample 81590. In addition, the pot life of the above adhesive was only about one half of that found for the MOCA-cured prepolymer, 25 minutes compared to 44. This information indicates that steric hindrance of the amine function does not influence the reaction rate as extensively as does the basicity of the amine. The base strength of 2-bromoaniline is greater than that of 2-chloroaniline.

Further evidence for the fact that base strength rather than steric hindrance governs reaction rate was found when an attempt was made to use 3,3',5,5'-tetraethyl-4,4'-diaminodiphenylmethane, m.p. 83-84°C, as a curing agent. This amine, when used in the molten state, gave a gel in less than one minute when mixed with a 1350 molecular weight prepolymer.

Three chlorinated analogues of MOCA were tested. These curing agents, 4,4'-methylenebis(2,6-dichloro-, 2,5-dichloro- and 2,3-dichloroaniline) were added to the prepolymer as solids (dust to 5.9 mils) and cured the same day as prepared. Further discussion of this mixing technique will be given in the next section. The immediate cure was utilized to prevent any significant reaction of the adhesive with moisture. In addition the application of heat was necessary to assist in dissolving the diamines in the prepolymer, 2,4-tolylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol. Only 4,4'-methylenebis(2,5-dichloroaniline) complete dissolved in the prepolymer on application of heat. However, the adhesive strengths obtained at 150°C were not sufficient even though the Vicat softening temperature was comparable to that obtained with a MOCA cure. Much longer pot lives of all three formulations were obtained than with MOCA under the same conditions. These data are given in Table 14 (Samples 81619, 81621 and 81623).

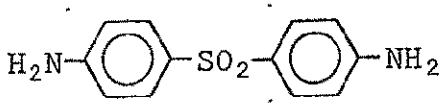
A curing agent, 4,4'-methylenebis(2-trifluoromethylaniline), reported to react about one sixth as fast as MOCA (Ref. 12) was tested. It was used to cure three polyoxytetramethylene glycol-based prepolymers. The pot life was estimated to about 9 times greater as compared to similar MOCA-cured prepolymers. The data obtained are given in Table 14 (Samples 81644, 90782 A, B and C and 90789). At -196°C, all but one set of specimens broke before testing. When attempts were made to determine the Vicat softening temperature, the samples cracked after 0.1 to 0.2 mm indentation. This indicated a low molecular weight polymer, a fact which was confirmed when it was found that the polymers readily dissolved in dimethylformamide at room temperature.

Evidently the basicity of this amine is so low that significant reaction is not obtained even at 110°C after 48 hr. This amine could not be titrated with perchloric acid in acetic acid (the method usually used to titrate aromatic amines). This is further evidence of its low basicity. It appears probable that, in order to get adequate cure, temperatures in excess of the target maximum (120°C) would be required.

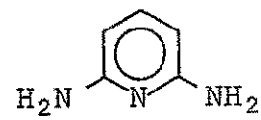
Holland, et al. (Ref. 13) described work with a urethane prepolymer curing agent which reacts much slower than MOCA. From their description the curing agent apparently was Curlaon L, a product sold by Naugatuck Chemical Company. A sample of this material was obtained and tested. It was treated in the manner reported by Holland. Excellent -196°C and 23°C tensile shear and T-peel strengths can be obtained, but the elevated temperature strengths are poor even after a 4-day cure at 75°C. These data are given under Samples 81573 and 81574 of Table 14.

The bis(*p*-aminobenzoate) of triethylene glycol was prepared and used to cure a 2,4-tolylene diisocyanate-terminated 1010 molecular weight polyoxytetramethylene glycol. The low 150°C strengths reflect the almost fluid nature of the polymer at this temperature (Table 14, Sample 90790).

Two other amines expected to exhibit low reactivity were tested. These are shown below:



4,4'-diaminodiphenylsulfone



2,6-diaminopyridine

Only 4,4'-sulfonyldianiline gave a polymer which had useful adhesive strength even at room temperature. At elevated temperatures both polymers were essentially fluid. The use of 2,6-diaminopyridine gave a low strength polymer due mainly to undissolved curing agent. An attempt was made to add this curing agent (m.p. 119-120°C) as a liquid. However, a rapid gelation occurred during mixing.

5. Physical Methods for Increasing Pot Life. A physical method for increasing the pot life of a MOCA-cured 2,4-tolylene diisocyanate-terminated polyoxytetramethylene glycol adhesive was investiated. This method involved the incorporation of MOCA as finely divided particles. Some reaction occurred; however, the rate was considerably slower than when molten MOCA was employed because the

Table 14

EFFECT OF CURING AGENT STRUCTURE ON BOND STRENGTH OF POLYURETHANE ADHESIVES[1]

SAMPLE NO.	PREPOLYMER COMPOSITION		% A-187[2]	CURING AGENT	APPROX. POT LIFE, min[3]	CURE CONDITIONS		TENSILE SHEAR STRENGTH, psi			T-PEEL STRENGTH, piw			VICAT SOFTENING TEMP., °C
	GLYCOL	ISOCYANATE				TEMP., °C	TIME, hrs	-196°C	23°C	150°C	-196°C	23°C	150°C	
71436	PM 620[4]	TDI[5]	0.5	MOCA[6]	9	75	24	MF[7]	3030	1405	45	13	46	
66102	PM 1000[8]	TDI	0.5	MOCA	44	75	24	MF	1800	1385	25	24	49	
81590	PM 1010[9]	TDI	0.5	MOBA[10]	25	75	72	4175	4085	470	26	106	11	165
81623[11]	PM 620	TDI	0.5	3-DCMA[12]	70	75	48		2800	1190		63	31	188
81621[11]	PM 620	TDI	0.5	5-DCMA[13]	35	75	48		5200	670		65	6	170
81619[11]	PM 620	TDI	0.5	6-DCMA[14]	>190[15]	100	24		3000	330		38	11	
81644	PM 620	TDI	0.5	MOTA[16]	84	104	48		2530	530		<1	<1	157
90782A	PM 1010	TDI	1.0	MOTA		90	24			450			3	150
B	PM 1010	TDI	1.0	MOTA		90	48			505			1	160
C	PM 1010	TDI	1.0	MOTA		90	72			460			1	157
90789[17]	PM 1010	MDI[18] TODI[19]	1.0	MOTA		110	48	2200	3530	320	10	77	5	160
90788[17]	PM 1010	MDI TODI	1.0	MOCA		75	24	MF	4260	970	17	72	77	170
90792	PM 1010	DMMDI[20]	1.0	MOTA		110	48	830	220	395	3	85	1	190
81573	PM 620	TDI	0.5	Curalon L[21]		75	24	1800	5000	45	5	11	5	50
81574	PM 620	TDI	0.5	Curalon L		75	96	6700	5070	260	28	50	11	65
90790	PM 1010	TDI	1.0	DATEG[22]		75	24	3530	2100	0	17	60	0	

[1]Aluminum was etched in standard chromic acid bath at 70°C for 10 minutes. Primer was 1.0% ethanolic solution of N-(trimethoxysilylpropyl)ethylenediamine
[2]A-187, γ-glycidoxypropyltrimethoxysilane, Union Carbide Co.
[3]Pot life determined by technique given in the Experimental Section
[4]PM 620, Polymeg 620, Quaker Oats Company (620 molecular weight polyoxytetramethylene glycol)
[5]TDI, 2,4-tolylene diisocyanate, DuPont
[6]MOCA, 4,4'-methylenebis(2-chloroaniline)
[7]MF, metal failure at pin hole grips
[8]PM 1000, Polymeg 1000, Quaker Oats Company (1000 molecular weight polyoxytetramethylene glycol)
[9]PM 1010, Polymeg 1010, Quaker Oats Company (1010 molecular weight polyoxytetramethylene glycol)
[10]MOBA, 4,4'-methylenebis(2-bromoaniline)
[11]Curing agents were added to prepolymer as solids (dust to 5.9 mils). Test specimens were placed in oven within one hour after preparation
[12]3-DCMA, 4,4'-methylenebis(2,3-dichloroaniline)
[13]5-DCMA, 4,4'-methylenebis(2,5-dichloroaniline)
[14]6-DCMA, 4,4'-methylenebis(2,6-dichloroaniline)
[15]No viscosity change occurred during determination
[16]MOTA, 4,4'-methylenebis(2-trifluoromethylaniline), added in molten state (m.p. 83-84°C)
[17]Prepolymer prepared using 3 parts MDI and 1 part TODI
[18]MDI, 4,4'-diisocyanatodiphenylmethane, Mobay Chemical Company
[19]TODI, 3,3'-bitolylene diisocyanate, Upjohn Chemical Company
[20]DMMDI, 3,3'-dimethyl-4,4'-diisocyanatodiphenylmethane, Aldrich Chemical Company
[21]Curalon L, Naugatuck Chemical Company, a mixture of hindered aromatic diamines
[22]DATEG, bis(p-aminobenzoate) of triethyleneglycol

initial temperature was lower and the adhesive mixture was heterogeneous. The MOCA was ultimately dissolved in the prepolymer by the application of heat during cure. This approach to increasing pot life is reported in the patent literature (Ref. 14).

An initial experiment using MOCA ground to a particle size passing a 100 mesh screen showed that the MOCA would dissolve in a 2,4-tolylene diisocyanate-terminated 1020 molecular weight polyoxytetramethylene glycol prepolymer when heated to 75°C for 24 hours. The cure appeared to be complete at this time, as indicated by the adhesive strengths obtained in spite of a large number of bubbles present. It was later found that the bubbles could be eliminated by completely degassing the MOCA-prepolymer mixture. The strengths obtained were:

TENSILE SHEAR STRENGTH		T-PEEL STRENGTH	
@ -196°C	3470 psi	@ 23°C	54 piw
@ 23°C	1550 psi	@ 150°C	10 piw
@ 150°C	650 psi		

These results agreed with data obtained using the same prepolymer and molten MOCA. (Compare with Sample 71435 of Table 16, Section A.6).

The strengths obtained in the initial experiment encouraged further work and a more quantitative estimation of pot life. Several particle sizes of MOCA were prepared and mixed with a 2,4-tolylene diisocyanate terminated 620 molecular weight polyoxytetramethylene glycol. The pot lives of these mixtures were then determined using a Brookfield viscometer (Model HAF, number seven spindle, 10 rpm). The measurement of pot life began immediately after the mixing and degassing. The end point was taken as the time at which the mixture reached 200,000 cps. A molten MOCA-cured Adiprene L-100 mixture will reach this viscosity in about 60 minutes. The data obtained are shown in Table 15.

The data in Table 15 reveal that to obtain a pot life of two hours or more, the MOCA particle size must be 13.8 mils or larger. However, particles of this size settle out of the mixture. This settling was observed visually and was verified by the fact that samples containing particle sizes larger than 13.8 mils had tacky surfaces after curing 24 hours at 75°C. The samples with particle sizes between 7.0-13.8 mils did appear to cure completely in 24 hours at 75°C but did not become transparent. The sample containing the smallest particles and the one where molten MOCA was used did become transparent. Opaqueness was probably caused by heterogeneity due to the presence of unreacted MOCA.

Table 15

EFFECT OF MOCA PARTICLE SIZE ON ADHESIVE POT LIFE[1]

SAMPLE NO.	PARTICLE SIZE RANGE, mils	INITIAL VISCOSITY, cps[2]	VISCOSITY AFTER 120 min., cps	POT LIFE, min.[3]	REMARKS
71443-D	13.8 - 33.1	8,000	36,800	>120	Particles settled during test
71447	13.8 - 23.2	12,800	40,000	>120	Particles settled during test
71443-C	9.8 - 13.8	16,000	--	80	Slight settling during test
71443-B	7.0 - 9.8	13,600	--	40	No settling
71443-A	dust to 5.9	276,000	--	--	No settling
81557	molten	23,200	--	9	

[1]Composition: 12.7 g. solid MOCA in 50.0 g. of 2,4-tolylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol prepolymer (8.39% NCO).
[2]After complete degassing
[3]Time to reach 200,000 cps

The high initial viscosity obtained with the smallest particle size MOCA could possibly have been due, in part, to the MOCA acting as a filler. However, the initial viscosities obtained using the same particle size 4,4'-diaminodiphenylsulfone and 2,6-diaminopyridine were 10,400 cps and 11,200 cps respectively. This indicated that the high viscosity obtained with MOCA was due to reaction rather than filler effects.

It was also found that the pot life of a MOCA-cured 2,4-tolylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol could be doubled by changing the method of solid MOCA addition. This was done by adding the MOCA as a solid that had been screened to a particle size of 14-33 mils and then by passing the mixture over a three roll paint mill. This mill ground the MOCA to a particle size determined by the spacings of the rolls in the paint mill. When the spacings were set at 1 or 3 mils the pot life increased to about 20 minutes as compared to 9 minutes when molten MOCA is used. The adhesive strengths were not greatly changed by this technique., 150°C tensile shear strengths were somewhat lower and 150°C T-peel strengths slightly higher. This technique insured more uniform distribution of the solid MOCA in the prepolymer than obtained when the solid MOCA was simply stirred into the prepolymer.

6. Comparison of Polyurethane Adhesives. As a result of our first year's work two polyurethane adhesives were developed which came close to meeting the contract goals with respect to strength properties. These adhesives are MOCA-cured 2,4-tolylene diisocyanate-terminated 620 and 1000 molecular weight polyoxytetramethylene glycols (8.4 and 6.2% NCO, respectively) containing 0.5% γ-glycidoxypropyltrimethoxysilane as additive. In addition the aluminum substrates are primed with N-(trimethoxysilylpropyl)ethylenediamine. These adhesives were compared with the commercially available products Adiprene L-100 (4.2% NCO) and Adiprene L-167 (6.3% NCO) preparing all the adhesives under the same conditions and at the same time. The data obtained are shown in Table 16.

The 150°C tensile shear strength values for Samples 71433 and 71435 were lower than values previously obtained. Also the T-peel strengths at all three temperatures differed from those previously obtained for both adhesives with some values being higher and some lower as shown in Table 16 footnotes. These data indicated that the strengths obtained were not optimum for any of the four adhesives. However, since they were all prepared at the same time, a comparison of the four adhesives has some validity. It appears that the adhesive based on the 620 molecular weight polyoxytetramethylene glycol has the best overall strength properties.

Table 16

COMPARISON OF POLYURETHANE ADHESIVES[1]

SAMPLE NO.	PREPOLYMER COMPOSITION			CURING AGENT	BONDLINE THICKNESS, mil	TENSILE SHEAR STRENGTH, psi			T-PEEL STRENGTH, piw		
	GLYCOL	ISOCYANATE	% NCO			-196°C	23°C	150°C	-196°C	23°C	150°C
71,433	Adiprene L-100		4.20	MOCA	6-7	>5580[2]	2266	267[3]	22[4]	87[4]	17[4]
71,434	Adiprene L-167		6.30	MOCA	6-7	>7000[2]	2686	880	41	34	33
71,435	Polymeg 1020[5]	2,4-TDI	6.15	MOCA	6-7	>5200[2]	3500	503[6]	27[7]	75[7]	19[7]
71,438	Polymeg 620[8]	2,4-TDI	8.45	MOCA	7-8	>6300[2]	3030	1405	45	13	46

[1]Aluminum primed with 1% ethanolic solution of N-(trimethoxysilylpropyl)ethylenediamine
[2]Metal failed
[3]Previously obtained value was 410 psi
[4]Previously obtained values were 44 piw (-196°C), 80 piw (23°C) and 66 piw (150°C)
[5]Polymeg 1020, Quaker Oats Co. (a 1020 M.W. polyoxytetramethylene glycol)
[6]Previously obtained value was 1206 psi
[7]Previously obtained values were 25 piw (-196°C), 24 piw (23°C) and 49 piw (150°C)
[8]Polymeg 620, Quaker Oats Co. (a 620 M.W. polyoxytetramethylene glycol)

7. Effect of Various Adherend Surface Preparations. In earlier work we had shown that polyurethane adhesives could be prepared which had the required bulk physical properties to fulfill the contract goals (Ref. 4). However, difficulty was encountered when attempts were made to reproduce adhesive strengths. This same problem has plagued many workers attempting to bond aluminum with polyurethanes. Further investigation of the influence of various surface preparations was, therefore, carried out. This study was aimed at developing background information to be used when an adhesive formulation having the necessary pot life and bulk properties in the corresponding polymer was developed. The variables studied were: primer type, primer concentration, primer application method, type of rinse water used after etching and type of etch. This work was done prior to that discussed previously in Section A.1.c.

One technique of aluminum surface preparation was used extensively in this program. This consisted of degreasing the aluminum, etching in chromic acid at 70°C for 10 minutes followed by tap water and deionized water rinses. After air drying the aluminum was primed with a 1.0% ethanolic solution of N-(trimethoxysilylpropyl)-ethylenediamine (A-1120), the primer being applied by wiping.

The primer concentration of 1.0% A-1120 in ethanol was used extensively. Other concentrations of primer were tested, but most of these were less than 1.0%. Primer concentrations of 0.1, 0.5, 1.0, 1.5 and 2.0% were used to determine the effect on elevated temperature properties. The results (Samples 81612 and 81613 of Table 17) indicate that 1.0% primer concentration is near the optimum. A more extensive statistical study would, of course, be necessary to confirm this conclusion.

A quantity of A-1120 was purified by distillation and used as a primer to check the effect of primer purity. Only 150°C T-peel strength was significantly effected (Samples 81627 and 81612, Table 17).

The influence of operator variability in priming was checked with Sample 81627. No variation more significant than normally found with polyurethane adhesives was noted. The two individuals performing this experiment did most of the priming for this entire program.

Samples 81636 and 81637 show the results obtained when the aluminum was etched with a freshly prepared etching bath and one which had been used several times prior. No significant differences are evident.

Samples 81642 and 81643 are adhesives prepared from two new batch prepolymers. They were used as checks to insure that the new prepolymers were equivalent to those previously employed.

A new amino-functional silane, N-(dimethoxymethylsilylisobutyl)-ethylenediamine (Z-2-2023), was introduced by Dow Corning Corporation. On hydrolysis it will give a linear polymer rather than the crosslinked polymer obtained with the N-(trimethoxysilylpropyl)-ethylenediamine primer (A-1120). It was of interest to determine how the polymeric nature of the primer would influence adhesive strengths. This new primer was evaluated at concentrations from 0.1% to 1.0% in combination with a MOCA-cured 2,4-tolylene diisocyanate-terminated 1000 molecular weight polyoxytetramethylene glycol prepolymer (Table 17, Samples 81566, 81578 and 81579). It would appear that the linear primer Z-2-2023 gives the same adhesion at elevated temperatures but decreased adhesion at room temperature as coxpared to the A-1120 primer (Sample 71566C). Using mixtures of Z-2-2023 and A-1120 resulted in increased room temperature strengths and retention of the elevated temperature strengths (Samples 81579A and B).

The above method of silane primer application depends mainly on atmospheric moisture to hydrolyze the methoxy groups on the silane and convert the primer to a polymeric material. The use of a prehydrolyzed silane primer, reported in the past year (Ref. 13), is said to result in increased adhesion. We tested this primer, hydrolyzed γ-glycidoxypropyltrimethoxysilane, in attempts to utilize its benefits in this program. The primer was applied by the wipe and spray methods and was used in combination with three different polyurethane adhesives. The results obtained are given in Table 17.

Significant increases in room temperature, tensile shear strength were obtained. However, the 150°C tensile shear strengths were about the same as the values obtained with the A-1120 primer and the same adhesive. T-peel strengths were, in general, quite good at -196°C, 23°C, and 150°C. A comparison of Samples 81569, 81570, 81575 and 81577A and B with 81566C gives the data.

Holland (Ref. 13) has shown that residual acetic acid (from the primer) on the adherends is detrimental to bond strength. Consequently, an attempt was made to overcome this problem by using a difunctional acid, adipic acid. This should allow adhesion to both the substrate and the polymer. No difference in strengths over that obtained using acetic acid was found. These data are shown in Samples 81583A and 81583B of Table 17.

A primer marketed by Minnesota Mining and Manufacturing, EC 3901, for use on aluminum with their cryogenic adhesive was tested with a polyurethane adhesive. The results indicated that it was no better than the A-1120 primer (Table 17, Samples 81593 and 81594).

An epoxy acid, 10,11-epoxyundecanoic acid, has been tested as a primer. Acids normally adhere very well to metals. Therefore, the opportunity for obtaining strong bonding between the adhesive and metal with this epoxy acid appeared to be good. The results (Samples 81587 and 81588 of Table 17) show that better adhesion can be obtained with the aminosilane A-1120.

It was common practice early in this program to prepare etched lap shear and T-peel specimens and then store them in clean, dry containers (30 days maximum storage time) until needed. This practice was based on results obtained by Narmco while studying a MOCA-cured polyurethane adhesive for aluminum (Ref. 2). We later found indications that increased adhesion was obtained by preparing the etched aluminum and using it the same day.

The following experiment lead to the above conclusion. Four sets of tensile shear specimens were prepared each having a different treatment after the sodium dichromate-sulfuric acid etch. These treatments were: (1) rinse in tap water followed by a deionized water rinse, dry in air and store in dry, clean bottles for two weeks; (2) same as (1) except bond the panels within 6 hours after etching; (3) rinse in deionized water, dry in air and bond within 6 hours; (4) rinse in distilled water, dry in air and bond within 6 hours. The same A-1120 primer solution was applied to each, and the same adhesive formulation was used to bond specimens. The results obtained (Table 17, Samples 81562A and B, 81563 and 81564, respectively) indicate that treatment (2) results in the highest bond strengths at 150°C.

At the same time that the above tensile shear specimens were prepared, additional panels from each set were subjected over a period of 24 hours to the "water break" test described in the Experimental Section. This test gives a qualitative determination of surface cleanliness as indicated by visual observation of the degree to which an adherend is wet by a water drop. Initially the water drop spread almost completely on the panels from treatment (2), less completely on those panels receiving treatments (3) and (4) (which appeared to be equivalent) and much less on those panels receiving treatment (1). This order was maintained over the 24-hour test period during which time the water drops exhibited less spreading with each successive test. Only the panels receiving treatment (1) retained the same degree of spreading over the 24 hour period. These results correlated with the 150°C tensile shear strengths obtained.

In addition the water break test was applied to panels from each set which had been primed. The water drops did not spread at any time on the primed panels.

A second series of experiments similar to the above was run (Table 17, Samples 81582 A, B, and C, 81584 A and B, and 81585 A, B, and C). In contrast to the results from the first series of experiments, the storage of etched panels did not appear to be detrimental to bond strength. Although the reason for this difference is not known, fewer variables are introduced by using freshly etched metal. This procedure was routinely employed in future work. In addition, the use of freshly etched metal more closely duplicates the conditions encountered in production.

Many chemical surface treatments for aluminum have been studied by others, *e.g.*, Smith and Susman (Ref. 6), so only new treatment were included in this program. One new treatment has already been discussed in Section A.1.b. Another treatment that was studied briefly is discussed below.

Aluminum test panels were treated with a commercially available preparation for aluminum, Pasa Jell 105, (Semco Sales and Service, Los Angeles, California) as per the manufacturers instructions. The panels were then primed with the usual aminosilane, A-1120, and bonded with a MOCA-cured 2,4-tolylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol. The 23°C and 150°C tensile shear strengths were in the range usually found with this adhesive. However, the T-peel strengths at 23°C and 150°C were significantly higher than the expected results. The 23°C T-peel strengths, normally below 10 piw, were 23 piw and 33 piw, (Table 17, Samples 81618A, 81618B, 81612A and 81613A).

The influence of sandblasting and Pasa Jell 105 on bond strength was further evaluated in Sample 81640, Table 17. These specimens were all prepared using the same prepolymer and MOCA. The only variable was the surface preparation. In this case, the use of Pasa Jell 105, even in combination with sandblasting, did not give results much different from those obtained with the standard etch. These data further indicated that sandblasting and etching tend to increase T-peel strength while having little effect on tensile shear strengths. The reason for the discrepancy between the two experiments is not known.

Surface roughness measurements were taken on aluminum samples prepared at the same time as those used in the above adhesive tests. Values of 55 μ in. (Sample 81640B) and 59 μ in. (Sample 81640A) were found for sandblasted surfaces and a value of 16 μ in. was obtained for the etched and unetched surfaces. These data show that the sandblasted surface is about three times as rough. They also indicate that etching does not effect the surface roughness, but only the surface chemistry, a conclusion not supported by scanning electron microscopy (Section A.9).

Table 17

INFLUENCE OF ADHEREND SURFACE PREPARATION ON BOND STRENGTH OF POLYURETHANE ADHESIVES[1]

SAMPLE NO.	GLYCOL	SURFACE PREPARATION				ALUMINUM[6]	PRIMER	PRIMER CONC., %	APPL.	TENSILE SHEAR STRENGTH, psi			T-PEEL STRENGTH, piw		
		SB[2]	ETCH[3]	PJ 105[4]	RINSE WATER[5]					-196°C	23°C	150°C	-196°C	23°C	150°C
81600	PM 620[7]		X		De[8]	fresh	A-1120[9]	1.0	W[10]	MF[11]	4330	1430	42	9	52
81612A	PM 620		X		De	fresh	A-1120	1.0	W		4700	1800		9	41
B	PM 620		X		De	fresh	A-1120	0.5	W		4600	1560		8	44
C	PM 620		X		De	fresh	A-1120	0.1	W		4500	1190		7	45
81613A	PM 620		X		De	fresh	A-1120	1.0	W		4500	1790		4	40
B	PM 620		X		De	fresh	A-1120	1.5	W		4800	1920		3	32
C	PM 620		X		De	fresh	A-1120	2.0	W		4400	1960		4	37
81617A	PM 620		X		De	fresh	A-1120	1.0	W		4500	1610		4	78
B	PM 620		X		De	fresh	A-1120	0.5	W		4800	1630		6	72
C	PM 620		X		De	fresh	A-1120	0.1	W		5300	1200		10	53
81627A	PM 620		X		De	fresh	A-1120	1.0	W		5100	1570		8	55
B	PM 620		X		De	fresh	A-1120	1.0	W		4500	1540		5	35
81636	PM 620		X		De	fresh	A-1120	1.0	W		4850	1250		8	23
81637	PM 620		X		De	fresh	A-1120	1.0	W		4400	1210		6	30
81642	PM 620		X		De	fresh	A-1120	1.0	W	MF	4120	1560	40	8	67
81643	PM 650[12]		X		De	fresh	A-1120	1.0	W		4350	1170		14	49
81566A	PM 1010[13]		X		De	old	Z-2-2023[14]	1.0	W		1570	1145			29
B	PM 1010		X		De	old	Z-2-2023	0.5	W		1615	1200			37
C	PM 1010		X		De	old	A-1120	1.0	W		2430	920			22
81578A	PM 1010		X		De	fresh	Z-2-2023	0.1	W		1510	870		15	35
B	PM 1010		X		De	fresh	Z-2-2023	0.25	W		1990	820		14	48
C	PM 1010		X		De	fresh	Z-2-2023	0.5	W		2060	1140		10	45
81579A	PM 1010		X		De	fresh	Z-2-2023	0.5	W		3120	850		23	40
							A-1120	0.5							
B	PM 1010		X		De	fresh	Z-2-2023	0.25	W		3030	875		27	47
							A-1120	0.25							
81569	PM 1010		X		De	old	Hyd A-187[15]	1.0	S[16]	3025	4620	570		120	4
81570[17]	PM 1010		X		De	old	Hyd A-187	1.0	S	6570	4740	735		118	15
81575	PM 1010		X		De	fresh	Hyd A-187	1.0	S	6950	4620	800	69	50	43
81577A	PM 1010		X		De	fresh	Hyd A-187	0.2	S	6200	4250	780	40	74	40
B	PM 1010		X		De	fresh	Hyd A-187	0.2	W	5220	3230	700	30	53	17
81580	L-315[18]		X		De	fresh	Hyd A-187	0.2	S			1160			
81581	L-315		X		De	fresh	Hyd A-187	0.2	W		5100	1450			
81583A[19]	PM 620		X		De	fresh	Hyd A-187	0.2	S	4650	5450	970	12	20	12
B	PM 620		X		De	fresh	Hyd A-187	1.0	S	5000	5320	1000	10	15	14
81593[17]	PM 620		X		De	fresh	EC 3901[20]	--	W	5650	3150	970	9	26	27
81594	PM 620		X		De	fresh	EC 3901	--	W	5500	3100	530	33	31	17
81587	PM 1010		X		De	fresh	EA[21]	1.0	W	6420	3180	560	22	20	6
81588[22]	PM 1010		X		De	fresh	EA	1.0	W	4830	2270	405	16	9	3

(Continued on Next Page)

Table 17 (cont'd)

INFLUENCE OF ADHEREND SURFACE PREPARATION ON BOND STRENGTH OF POLYURETHANE ADHESIVES[1]

SAMPLE NO.	GLYCOL	SURFACE PREPARATION					PRIMER	PRIMER CONC., %	APPL.	TENSILE SHEAR STRENGTH, psi			T-PEEL STRENGTH, piw		
		SB[2]	ETCH[3]	PJ 105[4]	RINSE WATER[5]	ALUMINUM[6]				-196°C	23°C	150°C	-196°C	23°C	150°C
81562A	PM 620		X		De	old	A-1120	1.0	W			1720			
B	PM 620		X		De	fresh	A-1120	1.0	W			2190			
81563	PM 620		X		De	fresh	A-1120	1.0	W			1850			
81564	PM 620		X		Di[23]	fresh	A-1120	1.0	W			1860			
81582A	PM 1010		X		De	old	A-1120	1.0	W		4100	735		67	31
B	PM 1010		X		De	fresh	A-1120	1.0	W		3150	725		74	32
C	PM 1010		X		TW[24]	fresh	A-1120	1.0	W		3400	730			
81584A	PM 620		X		De	old	A-1120	1.0	W		4950	1640		14	20
B	PM 620		X		De	fresh	A-1120	1.0	W		4950	1590		15	49
81585A	PM 620		X		De	fresh	A-1120	1.0	W		4720	1620		16	44
B	PM 620		X		Di	fresh	A-1120	1.0	W		3930	1530		16	44
C	PM 620		X		TW	fresh	A-1120	1.0	W		5570	1370		24	39
81618A	PM 620	X		X	De	fresh	A-1120	1.0	W		4900	1560		33	61
B	PM 620	X		X	De	fresh	A-1120	1.0	W		4400	1520		23	49
81640B	PM 620	X		X	De	fresh	A-1120	1.0	W	5330	4430	1180	21	13	24
A	PM 620	X	X		De	fresh	A-1120	1.0	W	5800	5000	950	15	87	45
C	PM 620			X	De	fresh	A-1120	1.0	W	MF	3570	1120	36	9	32
81605[25]	PM 620		X		De	fresh	A-1120	1.0	W		4600	660		9	16
81606	PM 620		X		De	fresh	A-1120	1.0	W		2180	660		5	6
81607A	PM 620		X		De	fresh	Lysine[27]	0.5	W		3400	750		5	13
B	PM 620		X		De	fresh	Lysine	1.0	W		3300	870		1	17
C	PM 620		X		De	fresh	Lysine	2.0	W		2900	870		3	8

[1]Adhesives were HOCA-cured 2,4-tolylene diisocyanate terminated polyoxytetramethylene glycol prepolymers containing 0.5% γ-glycidoxypropyltrimethoxysilane except for Samples 81570 and 81588
[2]SB, aluminum sand blasted with 120 grit aluminum oxide at 40 psi and then degreased
[3]ETCH, standard sulfuric acid-sodium dichromate etch
[4]PJ 105, Pasa Jell 105 (applied with wire brush) Semco Sales and Service, Inc.
[5]Rinse water used following sodium dichromate/sulfuric acid etch
[6]Fresh = aluminum etched and used same day, old = aluminum etched at least two weeks prior to use
[7]PM 620, Polymeg 620, Quaker Oats Company (620 molecular weight polyoxytetramethylene glycol)
[8]De, deionized water
[9]A-1120, N-(trimethoxysilylpropyl)ethylenediamine applied in ethanol
[10]W = primer applied by wiping with a Kimwipe
[11]MF = metal failure at pin hole grip
[12]PM 650, Polymeg 650, Quaker Oats Company (650 molecular weight polyoxytetramethylene glycol)
[13]PM 1010, Polymeg 1010, Quaker Oats Company (1010 molecular weight polyoxytetramethylene glycol)
[14]Z-2-2023, Dow Corning Corporation, N-(dimethoxymethylsilylisobutyl)ethylenediamine (applied in ethanol)
[15]Hyd A-187, hydrolyzed γ-glycidoxypropyltrimethoxysilane. Primer prepared by mixing the necessary amount of a solution of 10 g A-187 in 100 g of 1% acetic acid with 90 g of methanol
[16]S = primer applied by spraying
[17]Adhesive contains 1 0% A-187
[18]L-315, Adiprene L-315, duPont Chemical Company, a urethane prepolymer, 9.35% NCO
[19]Adipic acid used in place of acetic acid in primer
[20]EC 3901, 3M Company, a primer for use with cryogenic polyurethane adhesives
[21]EA, 10,11-epoxyundecanoic acid, applied from chloroform
[22]No additive used in adhesive
[23]Di, distilled water
[24]TW, tap water
[25]Aluminum rinsed with 1% sodium dichromate solution following etch
[26]Aluminum rinsed with 5% sodium dichromate solution following etch
[27]Lysine applied from aqueous solution

Adsorption of various ions onto an adherend surface has been suggested as the cause for both increased and decreased adhesion in some adherend-adhesive combinations. The influence of residual sodium dichormate on adhesion of a polyurethane to aluminum was checked by using both a 1.0% and 5.0% sodium dichromate bath as the final rinse. Residual salts lowered the adhesion of the polymer to aluminum, as shown by the data for Samples 81605 and 81606 of Table 17.

An attempt was made to combine the high reactivity of an aliphatic amine (with isocyanate) and the strong coordinating ability of an acid (with a metal) into a primer. Lysine, a diaminoacid, was used as a primer at three concentrations, 0.5%, 1.0% and 2.5%. No improvements were obtained (Sample 81607).

8. Effect of Fiber Glass Fillers. As noted earlier in this report, the pot life and adhesive strength goals could be met with a 620 molecular weight polyoxytetramethylene glycol-based adhesive. The -196°C T-peel strengths obtained, 16-21 piw, barely meet the 20 piw goal. It was desirable, however, to have a better -196°C T-peel strength to insure a greater reliability. Since it had been reported (Ref. 6) that use of glass fabric in the bond line of a MOCA-cured Adiprene L-100 adhesive nearly doubled the -196°C T-peel strength, an investigation of the effect of glass fibers and fabric on bond strength was undertaken. A MOCA-cured, 2,4-tolylene diisocyanate-terminated 1000 molecular weight polyoxytetramethylene glyco adhesive was used in this study. The data obtained using various glass fillers are shown in Table 18.

Other data obtained using a 2,6-diethyl-*p*-phenylene diisocyanate-terminated prepolymer was discussed in Section A.1.f.

The use of an unsized glass fiber at a 20 weight percent level resulted in increased 23°C tensile shear strength and 23°C and 150°C T-peel strengths without much change in the other strength values (Samples 90767 and 90776A). Incorporating the fibers by milling on a three roll paint mill resulted in lower adhesive strengths (Samples 90776A and B). An examination of the adhesive after testing revealed a large number of small bubbles in the milled sample as compared to the stirred sample. The bubbles could have been due to either entrapped air or reaction with moisture while milling, or both. The use of a 50% filler level lowered the bulk strength of the polymer considerably (Samples 90803, 90801 and 90802).

The best glass fiber tested appeared to be 709 either unsized (Sample 90776A), A-1120 sized (Sample 90780) or A-187 sized (Sample 90781). In all three cases the -196°C and 23°C T-peel strengths increased while the 150°C tensile shear strength decreased.

No conclusions concerning the use of glass fibers 830, 832 or 851 (Samples 90777, 90778 and 90779, respectively) have been made, since the fiber lengths necessitated that they be milled rather than stirred into the prepolymer. Milling the prepolymer-fiber mixture resulted in a material which would flow, whereas stirring the mixture gave a thick, unpourable paste. However, milling introduced a considerable quantity of bubbles and, therefore, the reliability of the data was questionable.

A disadvantage encountered in using glass fibers is their adverse effect on pot life. Pot life was reduced from about 44 minutes to 25 minutes (20% filler) and 15 minutes(50% filler).

Three types of scrim cloth were also tested. The objective of increased -196°C T-peel strength was not realized and the 150°C tensile shear strengths were considerably lower than found with no filler (Samples 90807, 90809 and 90815). Sample 90814 is included for a comparison with Sample 90815, because a fresh lot of prepolymer had to be used.

9. Adherend Surface Examination. The successful bonding of aluminum surfaces prepared by several techniques prompted an investigation of these surfaces with the scanning electron microscope. It was of interest to know whether a correlation could be found between adhesive strength and/or reproducibility and the surface characteristics, which can be seen with the scanning electron microscope.

The scanning or reflectance electron microscope makes possible the ready examination of physical structures at magnifications of 20x to 50,000x. This microscope fills the very critical gap between conventional optical microscopy and electron transmission microscopy but neither duplicates nor supersedes these two instruments. The major advantages are an extremely high depth of field and the avoidance of the replica process present in conventional transmission electron microscopy. Confusion from artifacts that are introduced by the replica process is, therefore, avoided, and very intricate surfaces can be examined without loss of detail.

Scanning electron micrographs were taken of the various aluminum surfaces which had received the treatments discussed in Section A.1.b. These micrographs, two magnifications of each surface, are shown in Figures 2 through 6.

Figure 2 and 3 show the aluminum surface before and after treatment with the usual chromic acid etch. The holes visible in Figure 3 are the result of etching the precipitates present in the grain boundaries, these precipitates being selectively attached by the etchant. The very

Table 18

INFLUENCE OF FIBER GLASS FILLERS
ON BOND STRENGTH OF POLYURETHANE ADHESIVES[1]

SAMPLE NO.	GLASS FIBER[2] TYPE	SIZE	% [3]	TENSILE SHEAR STRENGTH, psi -196°C	23°C	150°C	T-PEEL STRENGTH, piw -196°C	23°C	150°C
90767	--	--	--	MF[4]	1900	1600	72	23	32
90766	701	cationic	20	MF	2500	1170	73	84	46
90776A	709	water bound	20	MF	3500	1540	78	63	42
B[5]	709	water bound	20	MF	2800	1090	34	40	20
90777[5]	830	silane medium	20	MF	4200	1850	59	96	29
90778[5]	832	unknown	20	MF	4170	1490	47	126	45
90779[5]	851	chrome-silane medium	20	MF	3530	1150	52	80	38
90780	709	A-1120[6]	20	MF	3300	1290	81	77	28
90781	709	A-187[7]	20	MF	3700	1180	97	82	28
90803[8]	709	water bound	50	MF	4170	585	53	92	19
90804[9]	709	water bound	50	3970	2770	440	10	89	2
90801	709	A-172[10]	50	MF	4100	790	58	96	22
90802[9]	709	A-172	50	3600	3370	440	11	121	2
90807	scrim	A-1120	--	MF	2700	520	13	96	9
90809	scrim	--	--	MF	2830	945	52	58	45
90814	--	--	--	MF	3630	1290	87	62	30
90815	scrim	A-172	--	MF	2870	853	59	58	32

[1]Adhesives were MOCA-cured 2,4-tolylene diisocyanate-terminated 1010 molecular weight polyoxytetramethylene glycols containing 1.0% γ-glycidoxypropyltrimethoxysilane additive. All fibers were stirred into the adhesive except as noted
[2]Glass fibers and scrim cloth obtained from Owens Corning Glass Company
[3]Percent given as weight percent based on amount of prepolymer used
[4]MF, metal failure at pin hole grip
[5]Glass fibers incorporated into the adhesive formulation by milling on a three-roll paint mill
[6]A-1120, N-(trimethoxysilylpropyl)ethylenediamine
[7]A-187, γ-glycidoxypropyltrimethoxysilane
[8]Prepolymer degassed both before and after fibers were added
[9]Adhesive formulation degassed after fibers were added
[10]A-172, vinyltris(2-methoxyethoxy)silane

small white spots are probably these same type of precipitates, while the large spots may be debris. Figure 4 shows the same surface as Figure 3 does, except that the aluminum was rinsed with ferrous sulfate. No differences can be detected.

Figures 5 and 6 show aluminum surfaces which have received the alkali-chromic acid treatment and the alkali-chromic acid-ferrous sulfate treatment. Apparently large holes are caused by selective attack by the alkali. The smaller holes present on the surface and within the large holes are probably the result of attack by the chromic acid in the same manner as before.

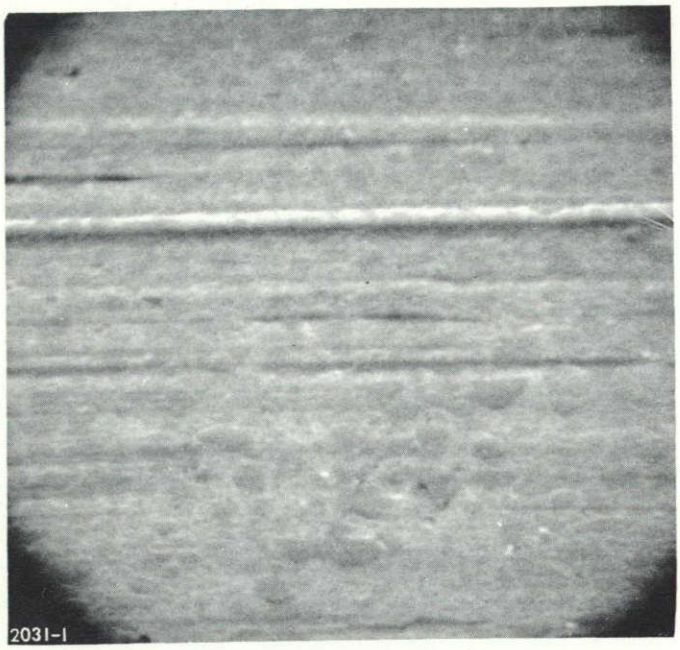
Although there are changes in the gross physical character of the surface, there is relatively little change in the adhesive strengths which were obtained. This lack of difference indicates that surface chemistry is a more controlling factor than is the surface geometry factor or that the different treatments do not change the total surface area enough to be reflected in different adhesive values. A more complete explanation would require further study.

It had been shown that some of the polyurethane adhesives studied had adequate tensile strength to provide the targeted tensile shear strengths, provided adequate adhesion to the aluminum was obtained.

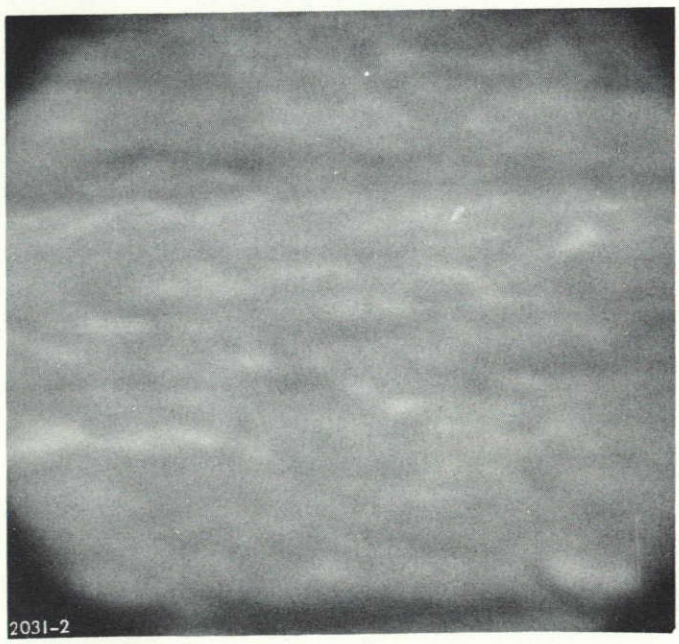
A study of primers resulted in increased adhesion, but apparently adhesive failure still occurred in tensile shear strength determinations at room temperature and above. The exact location of the failure was not known, however. The possible locations are the metal-primer interface, the primer-adhesive interface, or within the adhesive itself. In an attempt to determine the point of failure and help direct further research three samples were examined.

The samples examined were: chromic acid-etched aluminum; etched aluminum primed with a 2.0% ethanolic solution of N-(trimethoxysilylpropyl)ethylenediamine; and aluminum cut from a lap joint which had been tested to failure at room temperature and which visually exhibited adhesive failure.

The three samples examined appeared to be identical up to magnifications of 9200x. Two of these samples are shown in Figures 7 and 8. Since no differences could be seen, it was concluded that the primer could not be detected and that 100% adhesive failure was occurring. However, whether failure occurred at the metal-primer interface or at the primer-adhesive interface cannot be defined. Apparently no significant failure within the adhesive occurred.

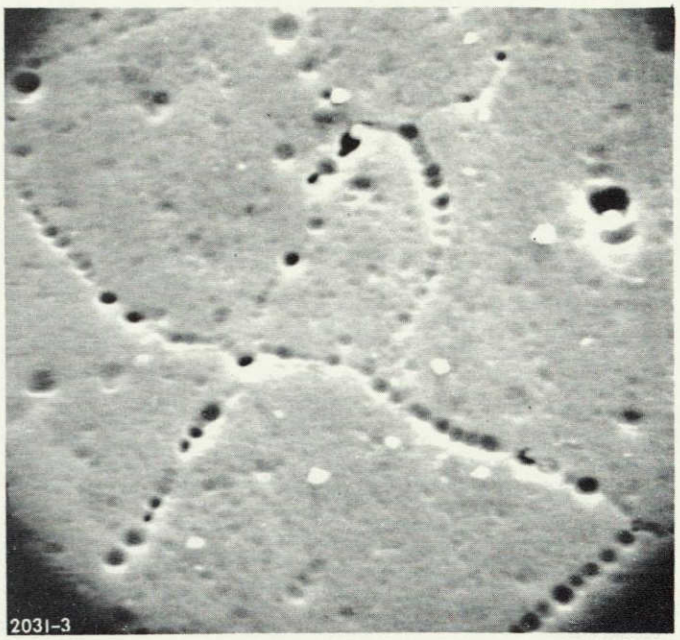


(1850x)



(9200x)

Figure 2. 2014-T6 Aluminum, no surface treatment



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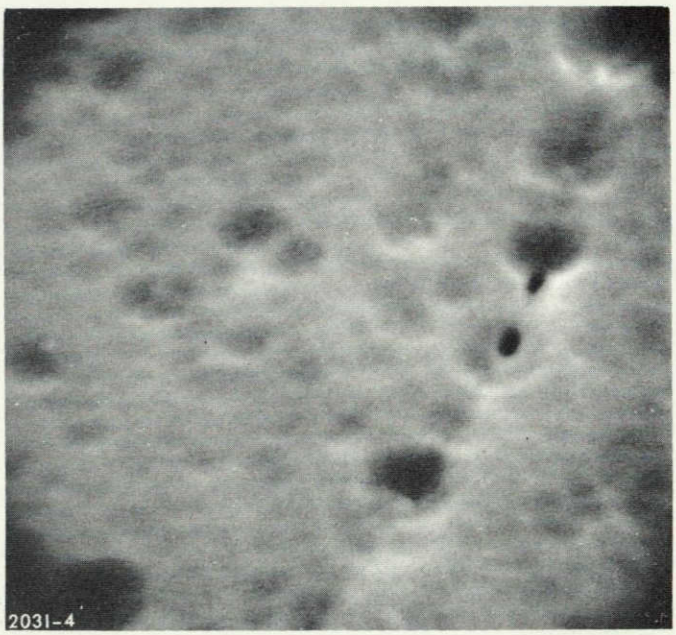
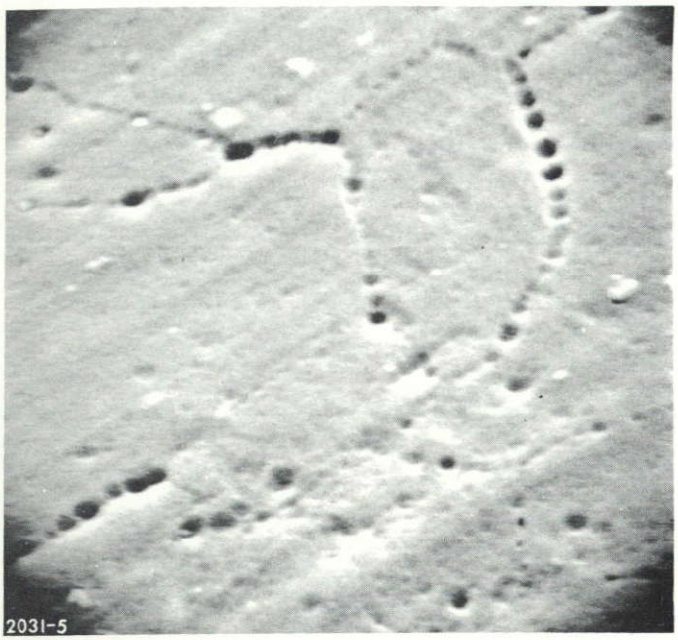


(9350x)

Figure 3. 2014-T6 Aluminum, chromic acid etch



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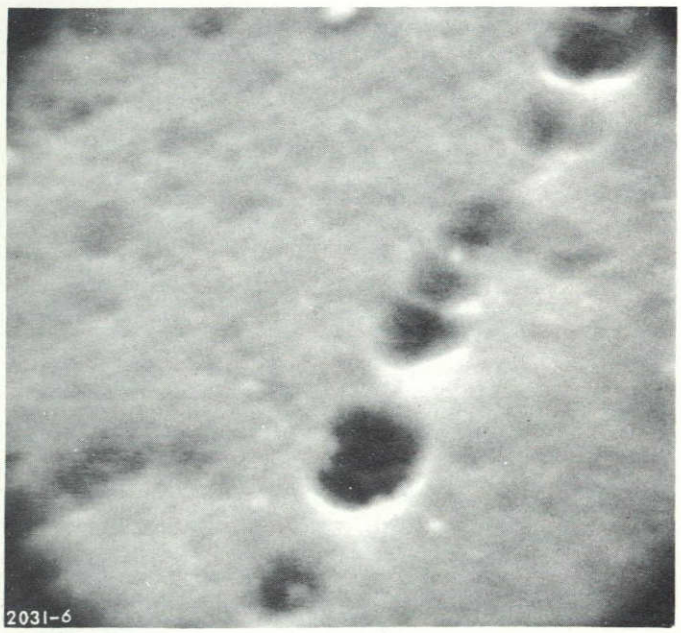
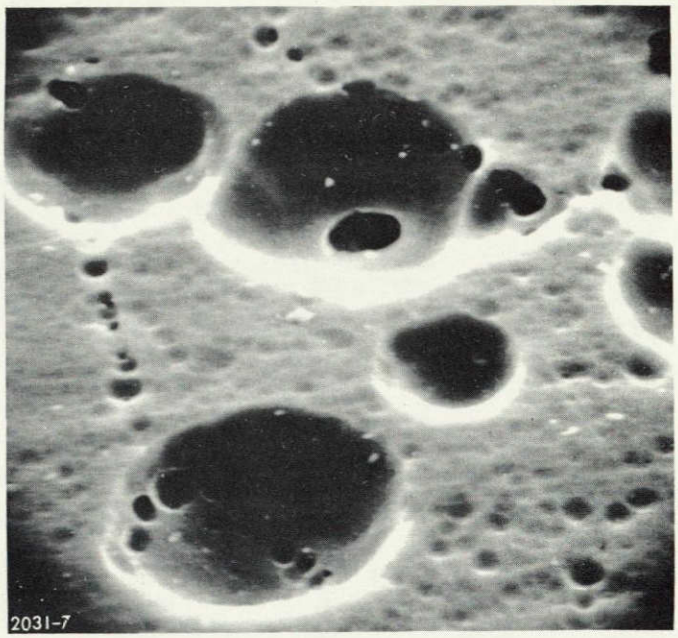


(9350x)

Figure 4. 2014-T6 Aluminum, chromic acid etch-ferrous sulfate rinse



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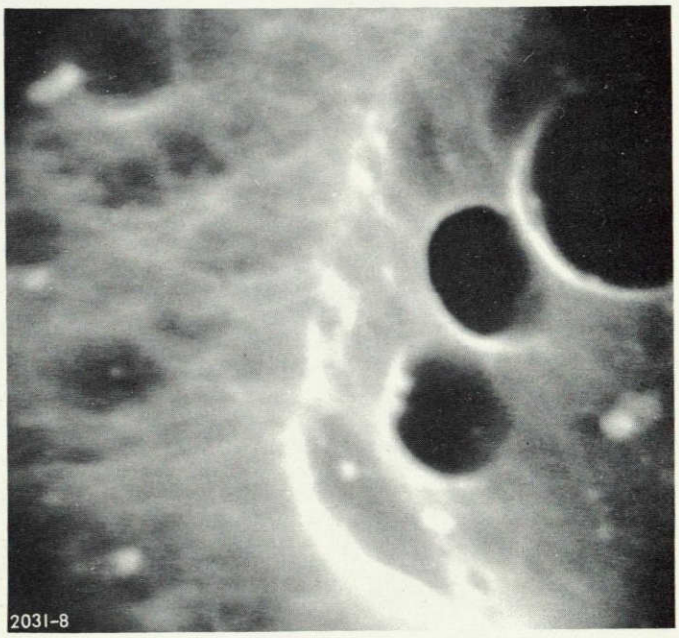
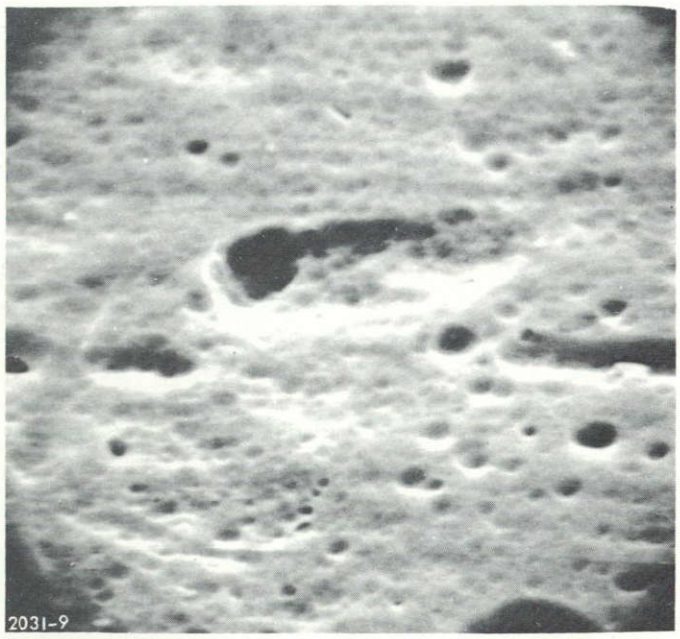


(9350x)

Figure 5. 2014-T6 Aluminum, alkali etch-chromic acid etch



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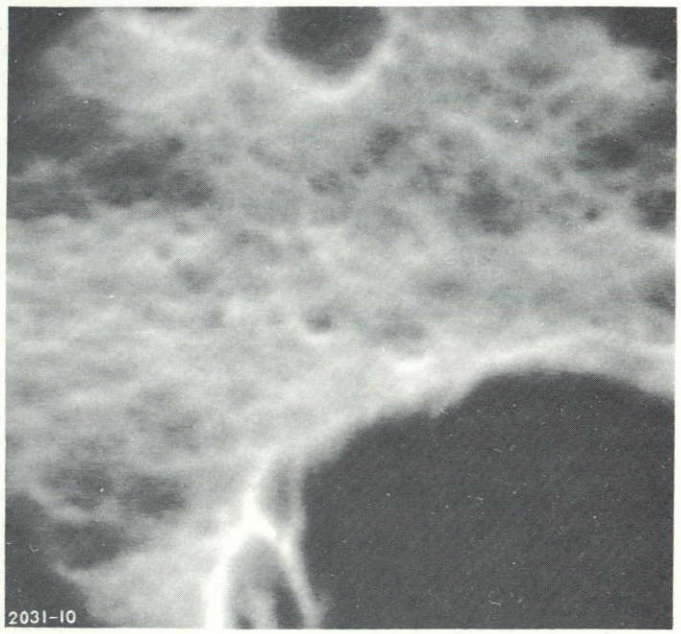
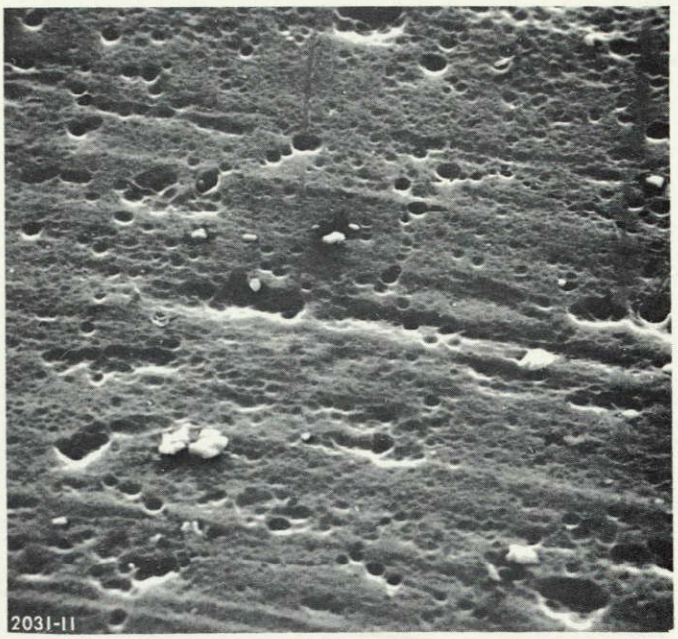
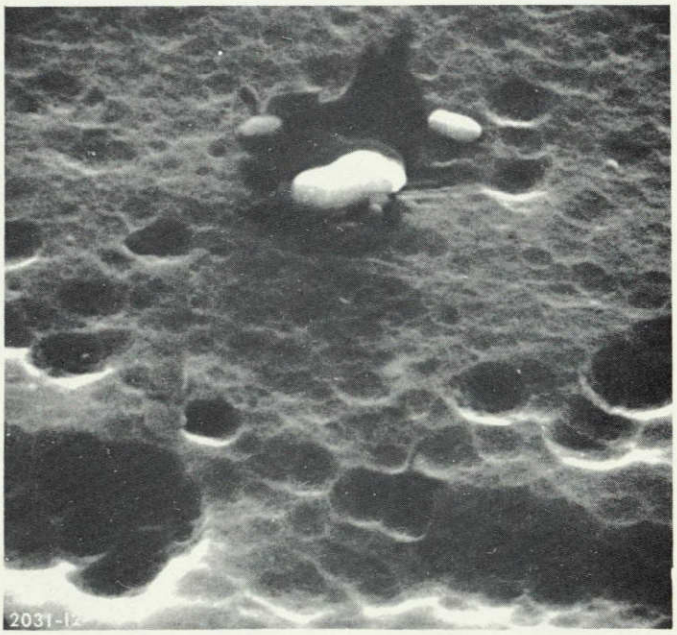


(9350x)

Figure 6. 2014-T6 Aluminum, alkali etch-chromic acid etch-ferrous sulfate rinse

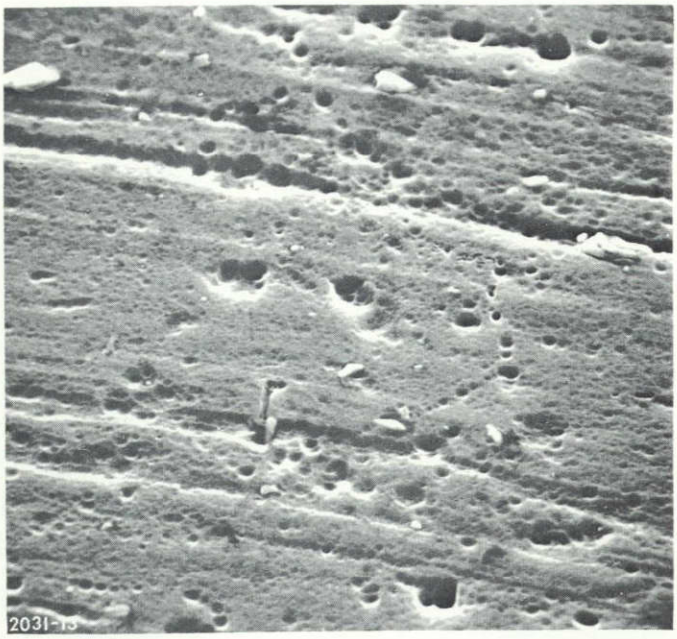


(1800x)

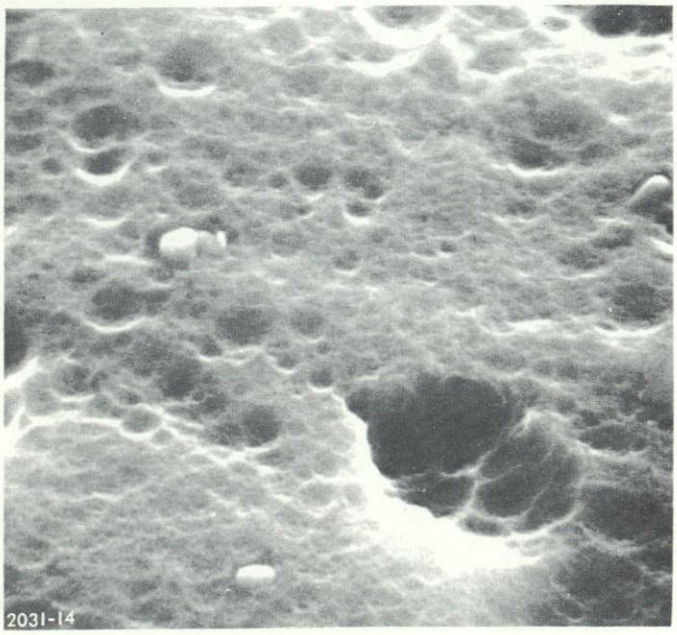


(8900x)

Figure 7. 2014-T6 Aluminum, primed with N-(trimethoxysilylpropyl)ethylenediamine



(2400x)

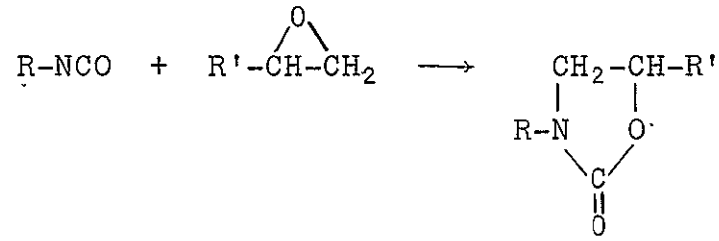


(9200x)

Figure 8. 2014-T6 Aluminum, lap joint tested to failure at room temperature

B. POLY-2-OXAZOLIDONE ADHESIVES

The 2-oxazolidone ring can be formed from reaction of an isocyanate with an epoxide:



This type of reaction is particularly attractive, in that it can combine in one system a urethane structure known to have good low temperature properties, plus epoxy moieties known to have good high temperature properties. The reaction of diisocyanates and diepoxides, to produce adhesives has been used previously (Ref. 15). However, with the catalysts employed temperatures of 160°C were required in order to obtain high conversions to the 2-oxazolidone structure (Ref. 16).

A program was undertaken to define the advantages and limitations of the poly-2-oxazolidones for adhesive use. This program was concerned with a definition of the influence of polymer structure on physical properties, particularly adhesive properties, and a search for catalysts to permit easier processing.

1. Catalysts. During the early stages of the work on poly-2-oxazolidones it was noted that the previously reported catalyst, tetramethylammonium iodide, was not soluble in the epoxy resin-diisocyanate mixtures. A search for better catalysts was therefore undertaken. A mixture of an epoxy resin, Epon 828, and a urethane prepolymer, either Adiprene L-315, or a 2,4-tolylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol, was used to evaluate potential catalysts. The rate of cure was followed by observing the disappearance of the isocyanate absorption in the infrared spectrum. Eighteen compounds were evaluated by this technique.

Most catalysts were evaluated using a cure temperature of 100°C. Cure studies at lower temperatures were carried out with significant cure found at temperatures as low as 50°C. Some cure evidently occurred even at room temperature (23°C) as evidenced by the viscosity increases noted on allowing adhesive formulations to stand under dry nitrogen. The cure temperature of 100°C was chosen to avoid long cure times.

The most effective catalysts found were tetrabutylphosphonium chloride, Bretol, Emcol CC-9, Emcol CC-36 and Emcol CC-42. Bretol is an alkyl (85% C_{16}, 15% C_{18}) dimethylethylammonium bromide from Fine Organics,

Inc. and the Emcols are polyalkoxytrialkylammonium chlorides from Witco Chemical Co. Tetrabutylphosphonium chloride was the most efficient, being about twice as effective on a weight basis as Emcol CC-36 or Bretol. It was also more effective on a molar basis, since Bretol has a molecular weight of 382 and tetrabutylphosphonium chloride has a molecular weight of 295. Adhesive mixtures prepared with tetrabutylphosphonium chloride gelled in about 30 minutes at 100°C, where the other catalysts required at least an hour.

All five catalysts were soluble in the adhesive mixture at 0.2 weight percent. The Emcols were much easier to handle, because they are liquids. All five compounds appeared to catalyze complete reaction in 24 hours at 100°C, as indicated by the infrared spectrum. No foaming was observed on the surface of cured polymers, indicating that these catalysts do not promote the water-isocyanate reaction. An added advantage found with Emcol CC-36 was its ability to lower the viscosity of the adhesive mixture from 11,400 cps to 8,000 cps.

The other catalysts tested were benzyltriphenylphosphonium chloride, methyltrioctylphosphonium dimethylphosphate, tetraethylammonium *p*-toluenesulfonate, tetraethylammonium acetate, HT-100 (stearyldimethylethylammonium bromide), stearyldimethylethylammonium iodide, ferric acetonylacetate, cuprous iodide, ferric chloride, tetrabutylammonium bromide, cetyltrimethylammonium iodide, decyldimethylphenylammonium iodide and cetyltributylammonium iodide.

Initially, stearyldimethylethylammonium bromide, a surfactant (HT-100) obtained from Fine Organics, Inc., was the most effective catalyst found. For this reason it was analyzed to determine its composition and to insure that trace contaminants were not acting as cocatalysts. Thin layer chromotography indicated at least four components. The contaminants were separated from the pure bromide by column chromatography on silica gel using benzene and methanol to elude the fractions. Two fractions, one containing all the contaminant and one the pure bromide, were obtained. NMR analysis indicated that separation was complete. A cure test using the contaminant (0.2% conc.) resulted in no cure after 3 days at 100°C. The purified bromide gave the same cure as found with the original material. The catalyst can also be purified by extraction of the contaminants with heptane.

A model compound was prepared from phenyl isocyanate and phenyl glycidyl ether using stearyldimethylethylammonium bromide catalyst. The known 3-benzyloxy-5-phenyl-2-oxazolidone was isolated from the reaction after 3 hours at 100°C, indicating that the desired 2-oxazolidone structure was being obtained with these catalysts.

2. Adhesives. A series of adhesives was prepared to better define the structures of the epoxy and isocyanate components required to give the maximum strength properties in a poly-2-oxazolidone. Five

epoxy resins, both aromatic and cycloaliphatic, and seven isocyanates, covering a wide range of molecular weights, were tested in various combinations. The same catalyst, stearyldimethylethylammonium bromide, was used in all the systems. The results are given in Table 19.

The best adhesive strengths were obtained with the bisphenol-A type of epoxy resin. The best combination of tensile shear and T-peel strengths was obtained using Epon 828 in conjunction with a 2,4-tolylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol prepolymer. The room-temperature, tensile shear strength of this system was rather low. However, it was increased by decreasing the average molecular weight of the prepolymer through addition of uncombined 2,4-tolylene diisocyanate as shown by the data for the first seven samples in Table 19. Acceptable -196°C tensile shear strength was also obtained with this adhesive system. However, the 150°C tensile shear strength was quite low.

In the above series of adhesives, a change from total cohesive failure to total adhesive failure at room temperature occurred with decreasing prepolymer molecular weight. This indicated that the bulk strength of the polymer was increasing with decreasing prepolymer molecular weight. When only 2,4-tolylene diisocyanate was used, a brittle polymer having low adhesive strength was obtained. This entire series of adhesives exhibited total cohesive failure at 150°C, indicating low strength polymers at this temperature.

Increasing the molecular weight of the epoxy segment by about 50% did not result in any significant change in tensile shear strengths (Samples 78494 and 65516 of Table 19).

Adhesives were prepared from Genepoxy 175, an essentially pure diglycidyl ether of bisphenol-A, and a series of diisocyanates. The results were similar to those for Epon 828 with the same diisocyanates, and it appears there is no added advantage in using Genepoxy 175.

A tetrafunctional epoxide, Epon 1031, was used to determine the influence of crosslinking. This solid epoxide was mixed with Epon 828 to obtain a fluid mixture and to facilitate handling. At the level tested (25 equivalent percent) the additional crosslinking does not appear to be beneficial. Epon 1031 was also dispersed in the prepolymer as a powder. At the cure temperature (100°C) Epon 1031 is a liquid and should diffuse into the prepolymer. The cured polymer showed presence of unreacted Epon 1031, indicating adequate diffusion had not occurred. Similar results were obtained using 50 equivalent percent of Epon 1031 in Epon 828.

The cycloaliphatic bisepoxide, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate (Unox 289), was used with a series of diisocyanates. Only low strength adhesives were obtained. The room temperature and 150°C tensile shear strengths and room temperature T-peel strengths were quite low. Interestingly, these adhesives exhibited mainly adhesive failure even at 150°C in the tensile shear tests, indicating that full use of the bulk strength has not been realized. However, cohesive failure was observed in the T-peel tests.

An examination of the data in Table 19 with respect to the structure of the diisocyanate shows that the best combination of lap shear and T-peel strengths are obtained when the polyether prepolymers are used. In fact, the use of these prepolymers appears to be required in order to obtain a significant T-peel strength.

During the investigation of various catalysts some lap shear and T-peel specimens were prepared and tested to determine any differences due to the catalyst used. The adhesive data are given in Table 20. A comparison of tetrabutylphosphonium chloride, the three Emcol catalysts and the Bretol catalyst indicated that all three give polymers with about equal 23°C tensile shear strengths when approximately equal cure times were used. A comparison of the data obtained when the Emcol CC-36 samples were cured for various periods of time (Samples 66526, 66519 and 66518-1) indicated that maximum cure was not obtained with all the other catalysts. The 23°C tensile shear strengths increased with longer cure times.

Better strengths could also be obtained with higher catalyst concentrations as shown by the data for Samples 66518-1 and 2. This was further support of the data obtained on longer cure times.

A series of tensile shear specimens was prepared and cured for various lengths of time at 100°C to determine minimum cure time (Table 20, Sample 65532). Infrared spectra were obtained at the same time intervals on a film of the same formulation. The presence of isocyanate could not be detected after 24 hours. However, maximum strength was not developed until somewhere between 24 and 48 hours

Other combinations of epoxy resins and diisocyanates were converted to poly-2-oxazolidone adhesives as given in Samples 65541, 65542 and 72466. No significant improvements were obtained, however.

Increased crosslinking was obtained by using Mondur MR (functionality about 2.2) in an adhesive formulation. An increase in tensile shear strengths at 23°C and 82°C and a large decrease in 23°C T-peel strengt resulted (Sample 72466, Table 20).

Table 19

EFFECT OF STRUCTURE ON BOND STRENGTH OF POLY-2-OXAZOLIDONE ADHESIVES[1]

SAMPLE NO.	MONOMERS		EQUIVALENTS	CURE TIME AT 100°C, hrs	TENSILE SHEAR STRENGTH, psi			T-PEEL STRENGTH, piw	VICAT SOFTENING TEMP., °C
	EPOXY	ISOCYANATE	EPOXY - ISOCYANATE		-196°C	23°C	150°C	23°C	
78494	Epon 828[2]	Polymeg 620-TDI[3]	0.10/0.10	141	>5200	1480	47	89	12
78503-A	Epon 828	Polymeg 620-TDI plus 5% TDI	0.10/0.095/0.005	66	4000	575	55	29	--
78503-B[4]	Epon 828	Polymeg 620-TDI plus 5% TDI	0.10/0.095/0.005	66	3640	1710	55	29	--
78506-A	Epon 828	Polymeg 620-TDI plus 10% TDI	0.10/0.09/0.01	64	5600	1660	89	66	--
78506-B[4]	Epon 828	Polymeg 620-TDI plus 10% TDI	0.10/0.09/0.01	64	5760	1920	61	37	--
78534	Epon 828	Polymeg 620-TDI plus 50% TDI	0.05/0.025/0.025	92	4000	2805	99	20	--
65521	Epon 828	Polymeg 620-TDI plus 75% TDI	0.175/0.045/0.13	89	940	3070	100	1	--
78509	Epon 828	Isonate 143L[5]	0.10/0.10	93	1100	1713	262	0	153
78511	Epon 828	HMDI[6]	0.10/0.10	90	390	805	61	5	60
78515	Epon 828	Adiprene L-315[7]	0.05/0.05	89	4040	1733	78	9	--
65516	Epon 836[8]	Polymeg 620-TDI	0.037/0.037	65	>6400	1490	57	32	--
78536	Genepoxy 175[9]	TDI[10]	0.10/0.10	93	138	565	127	0	--
78538	Genepoxy 175	Isonate 143L	0.10/0.10	91	1070	1650	179	<1	--
78540	Genepoxy 175	HMDI	0.10/0.10	92	360	480	31	3	--
78496	Genepoxy 175	Polymeg 620-TDI	0.025/0.025	117	5020	1590	50	45	--
78542	Genepoxy 175	Polymeg 1010-TDI[11]	0.025/0.025	91	3830	353	25	32	--
78544	Genepoxy 175	Adiprene L-315	0.05/0.05	91	2730	2766	30	56	--
78546	Epon 1031[12] Epon 828	TDI	0.025/0.075/0.10	98	185	436	64	0	--
78548	Epon 1031 Epon 828	Polymeg 620-TDI	0.0125/0.0375/0.05	98	4965	786	48	74	--
65512	Epon 1031 Epon 828	Isonate 143L	0.025/0.075/0.10	65	broke on cooling	840	15	0	--
65514	Epon 1031 Epon 828	HMDI	0 025/0.075/0.10	71	665	2420	120	1	--
78517	Unox 289[13]	Adiprene L-315	0.05/0.05	93	3370	358	15	6	--
78519	Unox 289	Isonate 143L	0.10/0.10	94	605	992	52	<1	--
78521	Unox 289	HMDI	0.10/0.10	60	- - no strength - -			--	--
78525	Unox 289	Polymeg 1010-TDI	0.04/0.04	67	1810	96	12	3	--
78527	Unox 289	Polymeg 381-TDI[14]	0.05/0.05	67	1940	152	29	5	--
78529	Unox 289	Polymeg 620-TDI	0.05/0.05	65	2800	98	35	4	--
78531	Unox 289	TDI	0.10/0.10	64	broke on cooling	447	65	<1	--

[1]Catalyst - SDEAB at a concentration of 0.2% of total charge (stearyldimethylethylammonium bromide)
[2]Epon 828 - Shell Chemical Co., epoxy equiv. = 185-192
[3]Polymeg 620-TDI, a 2,4-tolylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol
[4]Metal primer, A-1120, N-(trimethoxysilylpropyl)ethylenediamine
[5]Isonate 143L - Upjohn Chemical Co.
[6]HMDI - hexamethylene diisocyanate
[7]Adiprene L-315 - DuPont Chemical Co., (a urethane prepolymer with 9.35% NCO)
[8]Epon 836 - Shell Chemical Co., epoxy equiv. = 280-350
[9]Genepoxy 175 - General Mills, epoxy equiv. = 175
[10]TDI - 2,4-tolylene diisocyanate
[11]Polymeg 1010-TDI, a 2,4-tolylene diisocyanate-terminated 1010 molecular weight polyoxytetramethylene glycol
[12]Epon 1031 - Shell Chemical Co., epoxy equiv = 210-240
[13]Unox 289 - Union Carbide, epoxy equiv. = 210
[14]Polymeg 381-TDI, a 2,4-tolylene diisocyanate-terminated 381 molecular weight polyoxytetramethylene glycol

Table 20

EFFECT OF CATALYST ON BOND STRENGTHS
OF POLY-2-OXAZOLIDONE ADHESIVES

SAMPLE NO.	MONOMERS		CATALYST[1]	CURE TIME AT 100°C, hrs	TENSILE SHEAR STRENGTH, psi				T-PEEL STRENGTH, piw
	EPOXY	ISOCYANATE			-196°C	23°C	82°C	150°C	23°C
72453-2	Epon 828[2]	Polymeg 620-TDI[3]	TBPC[4]	68		2340			80
65524-1	Epon 828	Polymeg 620-TDI	CC-9[5]	22		1253			
66524-2	Epon 828	Polymeg 620-TDI	CC-36[6]	25		1795			
66524-3	Epon 828	Polymeg 620-TDI	CC-42[7]	20		1237			
66524-4	Epon 828	Polymeg 620-TDI	Bretol[8]	27		1841			
66526	Epon 828	Polymeg 620-TDI	CC-36	40		2206	215	121	
66519	Epon 828	Polymeg 620-TDI	CC-36	26	4220	1190	267	100	54
66518-1	Epon 828	Polymeg 620-TDI	CC-36	19		525			
66518-2[9]	Epon 828	Polymeg 620-TDI	CC-36	19		1220			
65532	Epon 828	Polymeg 620-TDI	CC-36	18 24 48 72 96		1460 1500 2065 1970 2020			
65541	DGB[10]	Polymeg 620-TDI	CC-36	50		590	140	110	7
72453-1	Epon 828	Polymeg 620-TDI	MTPD[11]	70		1560			
72453-3	Epon 828	Polymeg 620-TDI	BTPC[12]	66		650			7
65542	Epon 828	Polymeg 620-TDI	TETS[13]	70		1225	185	95	20
78500	Epon 828	Polymeg 620-TDI	SDEAI[14]	88	4140	1290		47	50
78498	Epon 828	Adiprene L-315[15]	SDEAI	90	4500	1620		20	47
72466	Epon 828	Polymeg 620-TDI Mondur MR[16] 1:3 ratio	CC-36	92		4300	900	105	2

[1]Catalysts used at 0.2 weight percent except for Sample 66518-2
[2]Epon 828, Shell Chemical Co., epoxy equivalent = 185-192
[3]Polymeg 620-TDI, a 2,4-tolylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol (8.45% NCO)
[4]TBPC, tetrabutylphosphonium chloride
[5]CC-9, Emcol CC-9, Witco Chemical Co. (polyalkoxytrialkylammonium chloride)
[6]CC-36, Emcol CC-36, Witco Chemical Co. (polyalkoxytrialkylammonium chloride)
[7]CC-42, Emcol CC-42, Witco Chemical Co. (polyalkoxytrialkylammonium chloride)
[8]Bretol, Fine Organics, Inc. [alkyl(85% C_{16}, 15% C_{18}) dimethylethylammonium bromide]
[9]1.0 Weight percent of catalyst was used
[10]DGB, 1,4-diglycidoxybutane
[11]MTPD, methyltrioctylphosphonium dimethylphosphate
[12]BTPC, benzyltriphenylphosphonium chloride
[13]TETS, tetraethylammonium *p*-toluenesulfonate
[14]SDEAI, stearyldimethylethylammonium iodide
[15]Adiprene L-315, a urethane prepolymer (9.35% NCO) DuPont Chemical Company
[16]Mondur MR, Mobay Chemical Co., a polymethylene polyphenylene isocyanate of about 2.2 functionality

Clash-Berg modulus temperature data and tensile strengths at four temperatures (from 23°C to 150°C) were obtained on two poly-2-oxazolidones. These measurements were made to determine the strength and temperature limitations of the polymers and to assist in evaluating the adhesion of these polymers to aluminum.

The adhesive tensile shear strength and bulk tensile strength data correlate well (Table 21). These data indicated that good use of the bulk strength of the polymer is being achieved, *i.e.*, good adhesion to aluminum is occurring, and the poor high temperature results are due to poor bulk porperties of the polymer at these temperatures. The benefit obtained by increasing the polymer chain stiffness is also evident.

Although poly-2-oxazolidones offer convenient adhesive formulations in terms of processing and pot life, the low strengths of the polymers at elevated temperatures present a serious drawback. Increasing the rigidity of the polymer backbone resulted in little increase in 150°C strengths. An attempt has been made, therefore, to increase the capability of the polymer to form hydrogen bonds, thereby increasing the cohesive strength of the polymers. An adhesive was prepared by reacting one mole of 2,4-tolylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol with one-half mole of Epon 828 and one-half mole of MOCA. In other words, a mixed urea-urethane-2-oxazolidone polymer was prepared. The data obtained with and without A-1120 primer are shown in Table 22. Although the cohesive strength of the polymer was increased as shown by the 23°C and 82°C strengths, the 150°C strength was still quite low. This formulation had a pot life of about 30 minutes, approximately three times as long as the comparable MOCA-cured prepolymer.

Table 22

POLY-2-OXAZOLIDONE ADHESIVES[1]
ON PRIMED AND UNPRIMED METAL

SAMPLE NO.	PRIMER[2]	TENSILE SHEAR STRENGTH, psi			T-PEEL STRENGTH, piw
		23°C	82°C	150°C	23°C
72458A	no	4550	574	166	43
72458B	yes	5040	980	160	48

[1]Adhesive was prepared from one mole 2,4-tolylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol mixed with one-half mole Epon 828 and one-half mole MOCA. Emcol CC-36 was used as the catalyst. Cure was 100°C for 48 hr

[2]A 1% ethanolic solution of A-1120 was used as the primer

Table 21

BULK PROPERTY DATA ON POLY-2-OXAZOLIDONES

SAMPLE NO.	STRENGTH, psi[1]	TEMPERATURE				CLASH-BERG DATA	
		23°C	55°C	82°C	150°C	T_{45000} °C	T_{675} °C
66532[2]	Tensile	2960	292	166	98	-21	+12
66526[2]	Tensile shear	2206		215	121		
66543[3]	Tensile	3725	1230	488	84	+16	+72
66543[3]	Tensile shear	3095	1495	598	120		

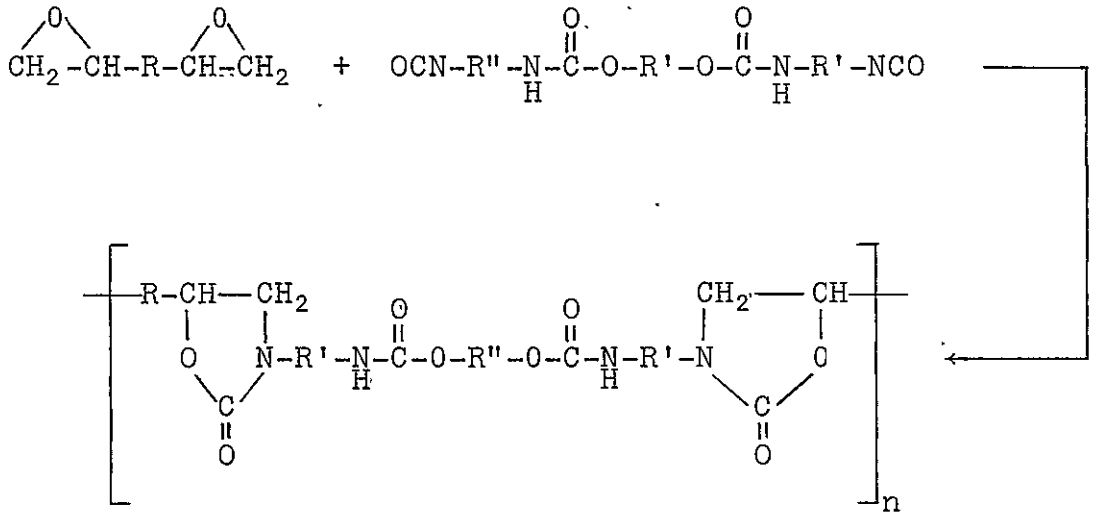
[1]Tensile strengths determined on 1.75-inch microdumbbells with a 0.004 sq. in. cross-sectional area

[2]Adhesive prepared from equimolar mixtures of Epon 828 and 2,4-tolylene diisocyanate capped 620 molecular weight polyoxytetramethylene glycol (8.13% NCO)

[3]Adhesive prepared from equimolar mixture of Epon 828 and a 3:1 ratio of 2,4-tolylene diisocyanate and a 2,4-tolylene diisocyanate capped 620 molecular weight polyoxytetramethylene glycol (8.13% NCO)

Two attempts were made to prepare the poly-2-oxazolidone of 1,4-diglycidoxybutane and 2,4-tolylene diisocyanate. It was expected that this polymer would not be as rigid as the comparable polymer formed with Epon 828. The reaction was very slow and could not be driven to completion, as indicated by infrared analysis. Only brittle products, probably of low molecular weight, were obtained.

The formation of a poly-2-oxazolidone from a diepoxide and isocyanate-terminated prepolymer ideally should proceed as shown below:



However, side reactions are also possible. Homopolymerization of the epoxide to a polyether could occur. Also trimerization of the isocyanates to isocyanurates is possible as is reaction of the isocyanates with the urethane function to give allophanates.

A series of experiments was performed to evaluate the possibilities of each of these side reactions and their contribution to polymer formation in a poly-2-oxazolidone. These results (Table 23) indicate that the major reaction is 2-oxazolidone ring formation. A small amount of allophanate formation may occur as well as some urethane formation (from the prepolymer and the free hydroxy groups in Epon 828). These latter reactions probably account for the apparent crosslinking indicated by the swelling tests discussed below.

3. Bulk Properties. Swelling tests were carried out on Sample 78500 in toluene, dimethylformamide and methyl ethyl ketone. The polymer swelled extensively in all three solvents but did not dissolve. Similar tests on the polymer used for Samples 78494 and 78496 of Table 19 also resulted in swelling, but no apparent dissolution appeared after four days at room temperature. The samples in all

Table 23

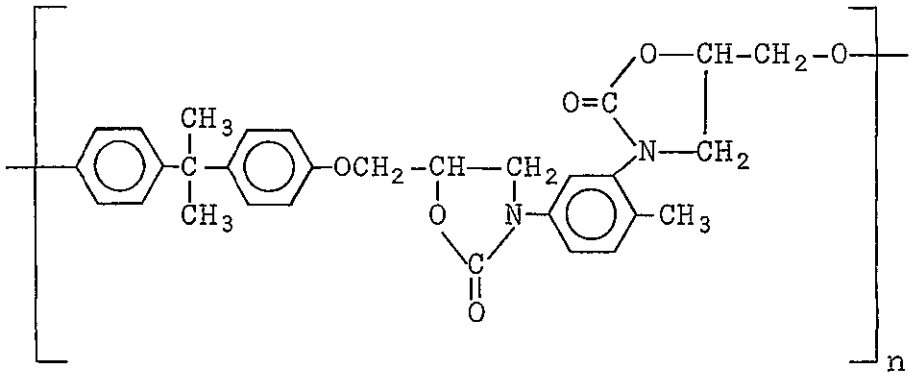
EFFECT OF EMCOL CC-36 ON POLY-2-OXAZOLIDONE COMPONENTS[1]

COMPONENT	CATALYST	RESULTS	CONCLUSION
Epon 828	CC-36	no reaction in 48 hours	no homopolymerization
Urethane prepolymer	none	gelled in 113 hours	allophanate formation
Urethane prepolymer	CC-36	gelled in 24 hours	allophanate formation
Phenyl isocyanate	CC-36	no reaction in 44 hours	no isocyanurate formation
Epon 828 and urethane prepolymer	CC-36	gelled in 1 hour	2-oxazolidone, allophanate and/or urethane formation

[1]Reactions run at 100°C in nitrogen atmospheres

cases retained their shape. We believe these polymers have usable linear chain length, relatively weak interchain bonding, and some crosslinking probably from allophanate and/or urethane formation, as just discussed.

A thermogravimetric analysis (TGA) was made on a polymer prepared from Epon 828 and 2,4-tolylene diisocyanate and catalyzed with stearyldimethylethylammonium bromide. This polymer, the structure of which is shown below, contains as its weakest link the 2-oxazolidone ring, and consequently the TGA should indicate a maximum



temperature at which polymers with the oxazolidone structure could be used. The TGA curve (in air) (Figure 9) indicates that the 2-oxazolidone structure should be stable at 150°C, the maximum temperature of interest in this project. Removal of the catalyst could possibly result in greater thermal stability.

Work on this phase of the program was discontinued because of the difficulties encountered in obtaining the desired strength at 150°C. The absence of strength at elevated temperatures is probably due to the lack of sufficient hydrogen bonding capability to give the necessary cohesive strength to the polymer.

C. EPOXY ADHESIVES

Even though an extensive technology exists on epoxy adhesives and though a large number of modifications have been tested (Refs. 6 and 15), an epoxy adhesive to meet the property and processing goals of this program was not available. In general, epoxy adhesives do not have the desired low temperature adhesive strengths nor the required toughness over the broad temperature range. Those epoxies which have the best strength and toughness, *e.g.*, the nylon-epoxies, require elevated temperature cures. However, in spite of the present state-of-the-art, further investigation of epoxy adhesives was warranted due to the available technology and the many approaches that had not been investigated. These approaches included adhesives prepared by

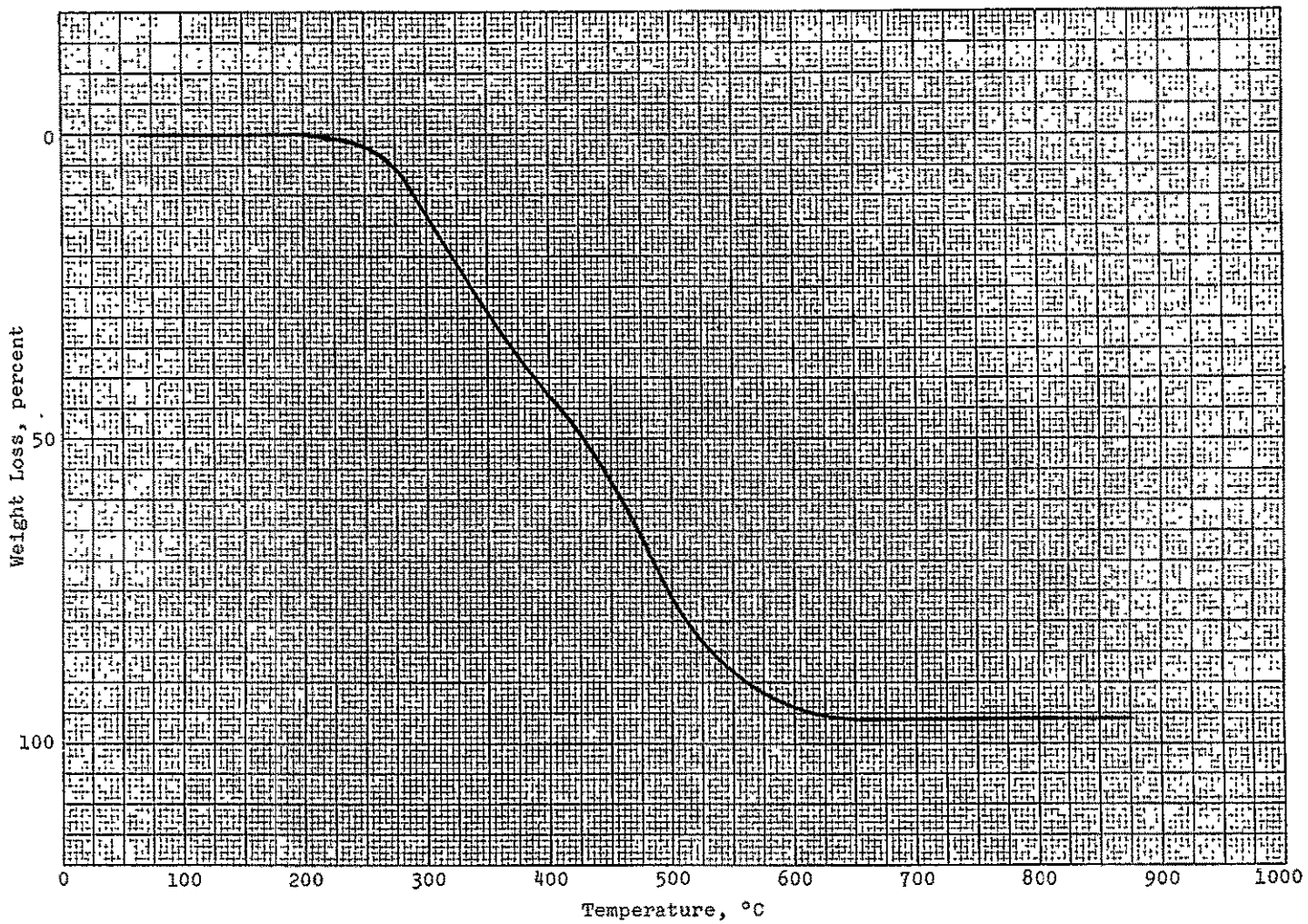


Figure 9. Thermogravimetric Analysis of poly-2-oxazolidone from Epon 828 and 2,4-tolylene diisocyanate (in air)

combination of available materials and adhesives prepared from newly synthesized materials.

Highly modified epoxy polymer have been found with good properties for use as resins for filament-wound cryogenic tanks (Ref. 17). Since these polymers had been shown to have good tensile strengths from room temperature to -253°C, it was of interest to evaluate the adhesive properties of some of the better materials. The two formulations shown below were chosen and bulk polymer samples prepared.

FORMULATION 1		FORMULATION 2	
Epon 828	110.0 gms	Epon 826	35.0 gms
Dodecenylsuccinic anhydride	115.9 gms	Epon 871	15.0 gms
Empol 1040 (trimer acid)	20.0 gms	Adiprene L-100	50.0 gms
Benzyldimethylaniline	1.0 gms	MOCA	27.6 gms

The polymer prepared from the first formulation shattered when cooled in liquid nitrogen while the second was unaffected even when struck with a hammer. Several variations of the second formulation were prepared to determine if the desired properties might be obtainable. These variations and the adhesive strengths shown by each are given in Table 24.

The best tensile shear strengths were obtained when the 1000 molecular weight urethane prepolymer was used. The best T-peel strengths were obtained with the 2000 molecular weight urethane prepolymer. The use of primer was most beneficial when the formulation contained a relatively large amount of urethane prepolymer. Sample 79397 gave the best tensile shear strengths, and it also contains the largest amount of low molecular weight urethane prepolymer. This indicates that the best properties would be obtained by making the adhesive formulation more like a urethane. The extreme of such a formulation is the polyurethane adhesives which have already been developed.

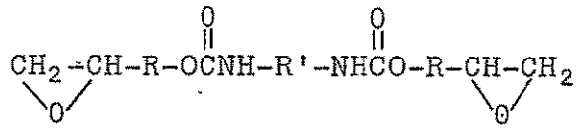
A variety of new epoxy resins and new amine curing agents was synthesized in an attempt to develop epoxy adhesives which would meet the objectives of this program. In addition, some of these materials could possibly be useful in the preparation of polyurethane and poly-2-oxazolidone adhesives. The selection of compounds to be prepared was based on their projected ability to impart toughness and ductility to an epoxy polymer. This was to be attempted by preparing polymers having high linearity and high capability for hydrogen bonding. Examples of the classes of materials shown below were selected for preparation.

Table 24

EPOXY-POLYURETHANE ADHESIVES[1]

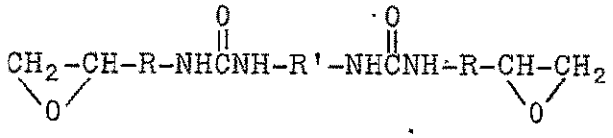
SAMPLE NO.	FORMULATION				PRIMER	TENSILE SHEAR STRENGTH, psi			T-PEEL STRENGTH, piw
	EQUIVALENTS EPON 826[2]	EQUIVALENTS EPON 871[3]	URETHANE PREPOLYMER	EQUIVALENTS PREPOLYMER		-196°C	23°C	150°C	23°C
79396	0.19	0.0175	L-100[4]	0.05	none	3020	3280	160	57
79400	0.38	0.0175	L-100	0.05	A-1120[5]	1130	2580	110	22
79399	0.19	0.035	PM 620[6]	0.05	A-1120	3730	5670	250	6
79398	0.38	0.035	PM 620	0.05	none	2630	4410	290	1
79397	0.19	0.0175	PM 620	0.10	A-1120	4120	6280[7]	520	14
79402	0.38	0.0175	PM 620	0.10	none	2830	5070	370	1
79403	0.19	0.035	L-100	0.10	none	1470	3320	70	84
79401	0.38	0.035	L-100	0.10	A-1120	4880	3820	175	24
79406	0.19	0.0175	PM 1000[8]	0.10	none	2710	3810	250	17

[1]All formulations were cured with MOCA (stoichiometric amounts) at 150°C for 5 hours
[2]Epon 826, Shell Chemical Co., epoxy equivalent 180-188
[3]Epon 871, Shell Chemical Co., epoxy equivalent 390-470
[4]L-100, Adiprene L-100, duPont Chemical Co. (a 2000 molecular weight urethane prepolymer)
[5]A-1120, Union Carbide Co., N-(trimethoxysilylpropyl)ethylenediamine (applied in ethanol)
[6]PM 620, a 2,4-tolylene diisocyanate terminated 620 molecular weight polyoxytetramethylene glycol, 8.35% NCO
[7]Metal failure occurred
[8]PM 1000, a 2,4-tolylene diisocyanate terminated 1000 molecular weight polyoxytetramethylene glycol, 6.15% NCO



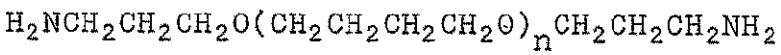
(I)

epoxyurethanes



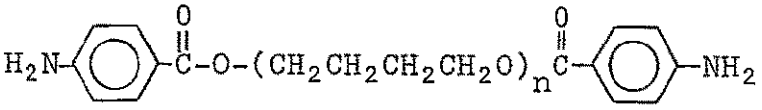
(II)

epoxyureas



(III)

aliphatic amine-terminated polyether

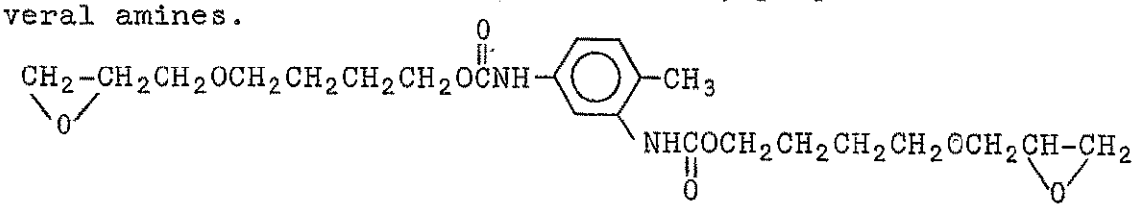


(IV)

aromatic amine-terminated polyether

Compounds of Type I were prepared by reacting various diisocyanates with epoxy alcohols. Two epoxy alcohols, glycidol and 4-glycidoxybutan-1-ol, were used. Compounds of Type II were to be synthesized by reacting diisocyanates with allylamine followed by epoxidation. Type III compounds are known. They are prepared by cyanoethylation of the corresponding glycol followed by reduction (Ref. 18). Compounds of Type IV were prepared by reaction of glycols with *p*-nitrobenzoyl chloride followed by reduction.

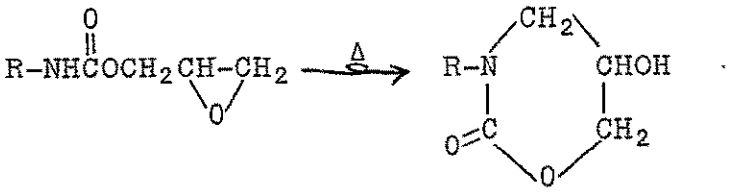
An epoxy resin of Type I, bis(4-glycidoxy-1-butyl) 4-methyl-*m*-phenylenedicarbamate (shown below), was readily prepared and cured with several amines.



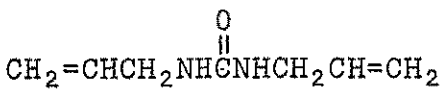
An adhesive prepared by curing bis(4-glycidoxy-1-butyl) 4-methyl-*m*-phenylenedicarbamate with 4,4'-methylenedianiline gave tensile shear strengths of 2090 (-196°C), 2670 (23°C) and 125 (150°C) and a 23°C T-peel strength of 1 piw. This adhesive has more of the characteristics of an epoxy than a polyurethane adhesive, *i.e.*, low -196°C tensile shear strength and low T-peel strength.

Curing the above epoxyurethane with diethylenetriamine resulted in a rigid and somewhat brittle polymer. This epoxyurethane was also cured with N,N'-di-*sec*-butyl-*p*-phenylenediamine and mixtures of N,N'-di-*sec*-butyl-*p*-phenylenediamine with *m*-phenylenediamine. The polymers obtained with these curing agents were high modulus, were less brittle, and able to withstand more flexing at room temperature than the more highly crosslinked polymers.

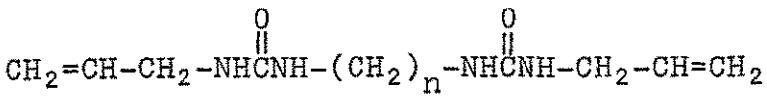
Attempts to react glycidol with diisocyanates did not give a usable product. The reaction did not proceed cleanly at 50°C, the temperature normally used in isocyanate-alcohol reactions. It is quite possible that rearrangement to a 5-hydroxytetrahydro-1,3-oxazine-2-one was occurring, as reported by Iwakura and Taneda (Ref. 19).



Three bisallylureas were prepared, and several unsuccessful attempts were made to epoxidize them to give epoxy resins of Type II. Epoxidation was attempted under both acidic (*m*-chloroperbenzoic acid) and alkaline (hydrogen peroxide, benzonitrile and potassium bicarbonate) conditions with only hydroxylated products being obtained. The bisallylureas prepared are shown below.



1,3-bisallylurea



n = 2 1,2-bis(3-allylureido)ethane
n = 6 1,6-bis(3-allylureido)hexane

The epoxidation of 1,3-diallylurea at room temperature under acid and alkaline conditions gave hydroxylated products. At low temperature, *e.g.*, 0°C, no apparent reaction occurs. Shorter reaction times at room temperature gave a product containing large amounts of olefinic and hydroxyl functionality. The desired epoxide is apparently quite reactive, thus making isolation difficult.

The preparation of aliphatic amine-terminated polyethers (Type III compounds) was attempted by cyanoethylation of 1,4-butanediol followed by reduction to give 1,4-bis(3-aminopropoxy)butane. Work on this preparation was discontinued even though experimental results indicated that it could be prepared. The data obtained by use of bis(3-aminopropoxyethoxy)ethane [H_2N-$CH_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2$-$CH_2OCH_2CH_2CH_2NH_2$], an aliphatic diamine of similar structure and molecular weight, indicated that the desired properties would probably not be obtained. A low modulus polymer was obtained when Epon 828 was cured with bis(3-aminopropoxyethoxy)ethane.

The bis-*p*-aminobenzoate of a 620 molecular weight polyoxytetramethylene glycol (a type IV compound), was prepared by reaction of the glycol with *p*-nitrobenzoyl chloride followed by reduction. The product was a medium viscosity oil and analyzed 3.63% NH_2 (theory 3.73% NH_2). This curing agent was used to cure the epoxy resins Epon 828 and bis(4-glycidoxy-1-butyl) 4-methyl-*m*-phenylenedicarbamate and a 2,4-tolylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol. All three polymers had low modulus even at room temperature.

The bis-*p*-aminobenzoate of triethyleneglycol was prepared to determine if a lower molecular weight diamine would give higher modulus products. This diamine, m.p. 104°C, was used to cure Epon 828 and a 2,4-tolylene diisocyanate-terminated 620 molecular weight polyoxytetramethylene glycol. The Epon 828-cured product was a hard clear polymer. Adhesive test indicated a brittle polymer. The polyurethane was flexible and tough. However, the 150°C tensile shear strengths were low.

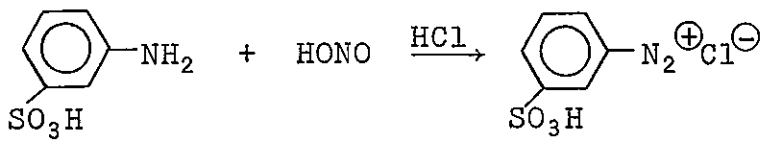
The diamine prepared from reduction of 1,4-butylenebis(*p*-nitrobenzoate) was shown to be only 70% pure. The melting point of this impure product was 178°C (dec). Because this high melting point, no further effort was expended on preparation of a purer product.

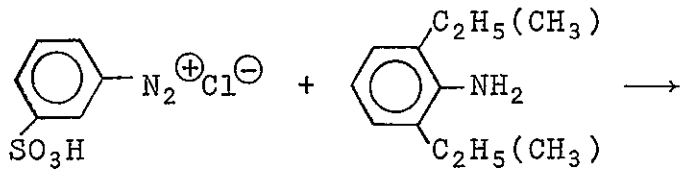
Work on preparation of new epoxy resins was discontinued when it was found that the new polyurethanes being prepared were very likely to produce the desired adhesives.

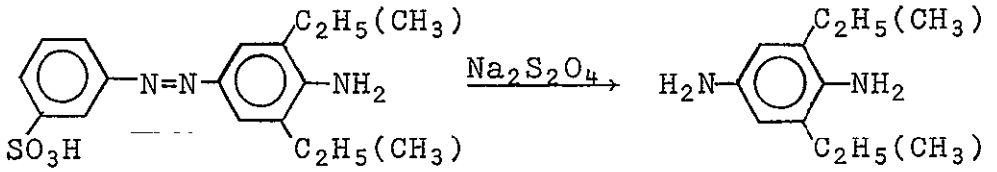
IV. EXPERIMENTAL

A. PREPARATION OF DIISOCYANATE PRECURSORS

1. 2,6-Diethyl- and 2,6-Dimethyl-*p*-phenylenediamine Dihydrochloride







The following procedure was used to prepare 2,6-diethyl-*p*-phenylenediamine dihydrochloride several times and was the best of several variations tried. The preparation of 2,6-dimethyl-*p*-phenylenediamine dihydrochloride was done on this scale only once.

A 12-liter flask equipped with a mechanical stirrer, thermometer and cooled in an ice-salt bath was charged with 3000 ml water and 150 ml concentrated hydrochloric acid. One mole (150 g) of 2,6-diethylaniline was added slowly with stirring.

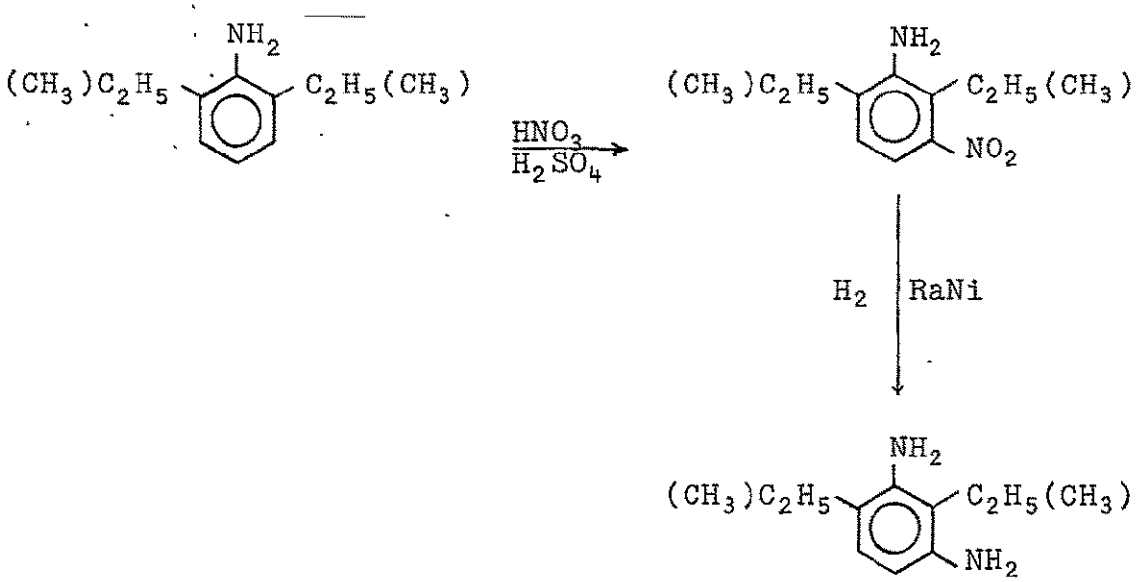
The diazonium salt of metanilic acid was prepared by quickly adding a solution of 74.5 g of sodium nitrite in 200 ml water (0-5°C) to a solution of 195 g of sodium metanilate in 1000 ml water (0-5°C). This solution was then poured quickly into 212 ml of concentrated hydrochloric acid in 600 g of ice. After standing for 15 minutes at 0-5°C the diazonium salt was added in a fine stream to the 2,6-diethy

aniline hydrochloride suspension prepared above. The addition was done at 0°C, and the reaction stirred one hour at 0°C after the addition was complete. An occasional addition of ice to the reaction flask was used to maintain the temperature at 0°C.

The reaction was then allowed to warm slowly to 15°C. A heating mantle was then used to heat the reaction. When the temperature reached 25°C, 140 g of sodium hydroxide in 400 ml water was added and a nitrogen blanket placed over the reaction. At 45°C, 215 g of sodium dithionite and 50 g of sodium hydroxide in 100 ml water were added. After 3-5 minutes another 215 g of sodium dithionite and 50 g of sodium hydroxide in 100 ml water was added. The reaction was heated to 80°C and then cooled with external cooling. When a temperature of 50°C was reached, 450 ml of chloroform was added and the reaction stirred vigorously under a nitrogen blanket. The chloroform layer was separated and the extraction repeated with another 450 ml of chloroform. The combined chloroform layers were stripped on a rotary evaporator, leaving a dark brown liquid which turns blue if exposed to air.

The crude amine was dissolved in 500 ml of absolute ethanol and the solution cooled in ice. The dihydrochloride was formed by slow addition of 225 ml of concentrated hydrochloric acid. The solid was filtered off and washed with absolute ethanol until the washings were clear. The white product was then dried in a vacuum at 50°C. Yields usually ranged from 57% to 62%. This is a modification of the procedure given in Ref. 7.

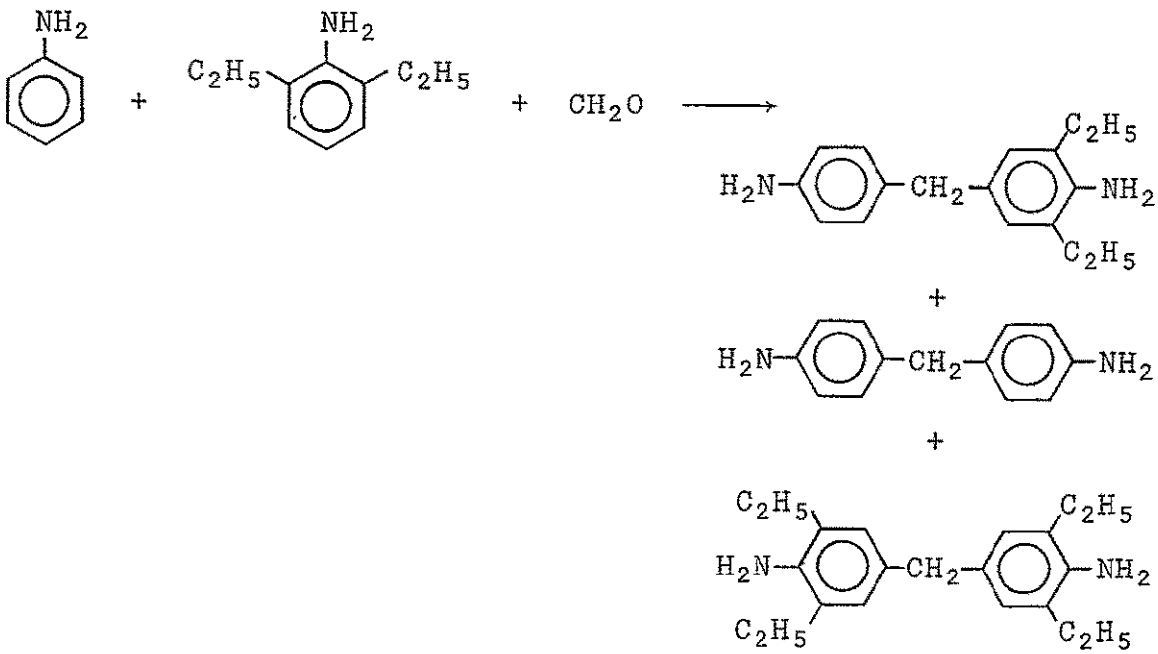
2. 2,4-Diethyl- and 2,4-Dimethyl-*m*-phenylenediamine Dihydrochloride.



a. 2,6-Diethyl- and 2,6-Dimethyl-3-nitroaniline. Keeping the temperature below 30°C, one mole of 2,6-dimethyl- or 2,6-diethylaniline was dissolved in 7.67 mole of concentrated sulfuric acid. This solution was cooled to 5°C, and a solution of 1.05 mole of 70% nitric acid in 1.0 mole of sulfuric acid was added dropwise keeping the temperature below 10°C. After the addition was complete, the reaction was stirred for one hour at 5-10°C and then poured onto 2 to 2.5 Kg of crushed ice. The pH was adjusted to 3-4 with concentrated ammonium hydroxide while keeping the temperature below 25°C. The mixture was then extracted with chloroform (3 x 150 ml). The crude nitroaniline was recovered by stripping off the chloroform on a rotary evaporator. NMR and IR spectra of the crude products indicated the presence of the meta isomer only and purities of greater than 95%. The crude yields were 99% and 97% respectively for the 2,6-dimethyl- and 2,6-diethyl-3-nitroaniline.

b. 2,4-Diethyl- and 2,4-Dimethyl-*m*-phenylenediamine Dihydrochloride. The crude nitroanilines from above were dissolved in 800 ml of tetrahydrofuran and reduced over 20 g of Raney nickel (W-4) at 50°C and 50 psi of hydrogen. The catalyst was removed by filtration and the solvent evaporated. The residue was taken up in methano and cooled to 5°C. Concentrated hydrochloric acid (2.5 mole) was added slowly. The precipitated salts were filtered off and dried. Yields were 76% and 98% respectively for the 2,4-dimethyl- and 2,4-diethyl-*m*-phenylenediamine dihydrochlorides.

3. 3,5-Diethyl-4,4'-Diaminodiphenylmethane Dihydrochloride

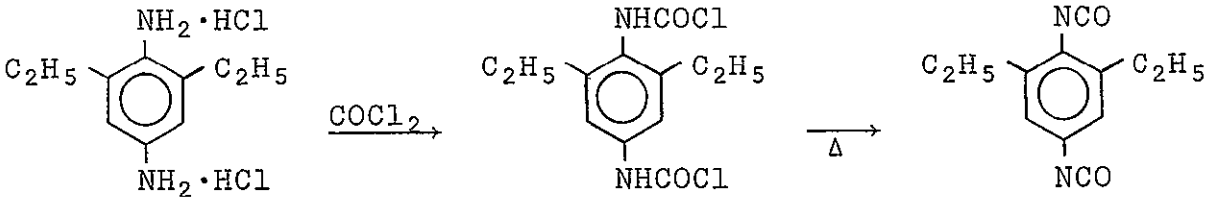


One and one half moles (224 g) of 2,6-diethylaniline was added to a solution of 565 ml of concentrated hydrochloric acid in 3000 ml of water. A precipitate of the aniline hydrochloride formed. Formaldehyde (37%, 210 ml) and aniline (420 g, 4.5 mole) were then added in one portion in that order. The precipitate dissolved on the addition of the aniline. The reaction was allowed to proceed at room temperature for five hours during which time a precipitate formed. The reaction mixture was then heated to 75°C and allowed to cool slowly to room temperature. The mixture was filtered to remove a precipitate which was shown by thin layer chromatography (TLC) to be 3,3',5,5'-tetraethyl-4,4'-diaminodiphenylmethane dihydrochloride. The filtrate was evaporated to about 1500 ml and then cooled. The solid which precipitated was filtered off and the wet filter cake recrystallized from 600 ml of 95% ethanol. The resulting precipitate was recrystallized a second time from 95% ethanol and the resultant product shown (by TLC analysis of the free amine) to contain only one component. When dried, the light yellow product weighed 96.0 g (19.5% yield).

B. PREPARATION OF DIISOCYANATES

All of the diisocyanates that had to be synthesized were prepared using the same general procedure. This procedure is given below for the preparation of 2,6-diethyl-*p*-phenylene diisocyanate.

1. 2,6-Diethyl-*p*-phenylene Diisocyanate

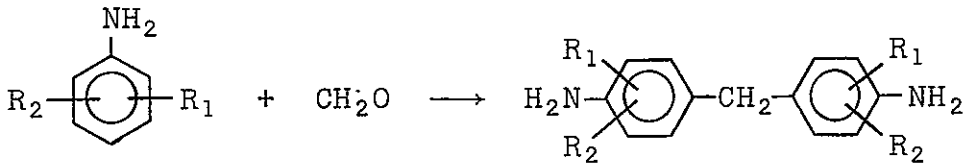


A nitrogen swept four-necked flask equipped with a stirrer, condenser, dry nitrogen inlet, thermometer, heating mantle, and gas dispersion tube adjusted to reach below the liquid surface was charged with distilled-dried *o*-dichlorobenzene (500 ml/100 g dihydrochloride). A 20% sodium hydroxide solution was used to trap the off gases. The dried, finely divided diamine dihydrochloride was transferred into the reaction flask under nitrogen. Agitation was begun and chlorine-free dry phosgene (passed through mineral oil and sulfuric acid) was added rapidly while the temperature rose to 40-46°C and then subsided. The flow of phosgene was reduced to maintain a slight positive pressure, and the temperature was increased to 120-125°C. The flow of phosgene was then increased to maintain a positive pressure and, therefore, the maximum reaction

rate. This condition was maintained until all the solid had entered solution. The flow of phosgene was again reduced to give a slight positive pressure and the reaction heated to 170-175°C and maintained for 2 hours. The addition of phosgene was then stopped and dry nitrogen passed through the solution which was held at 170-175°C for another one to one and one half hours. The reaction was then cooled to 120-130°C and filtered under vacuum and nitrogen through filter aid into a distillation flask. The majority of *o*-dichlorobenzene was removed on a rotary evaporator. The residue was fractionally distilled. The colorless distillate was analyzed for percent NCO and hydrolyzable chloride content.

The properties and analyses for each diisocyanate prepared are given below in Table 25.

C. PREPARATION OF SUBSTITUTED 4,4'-METHYLENEBIS(ANILINE)S



1. General Procedure. Glacial acetic acid (500 ml) and the appropriate aniline (0.2 mole) were charged to a reaction flask and HCl (30 ml) slowly added with stirring. The mixture was heated to 65 to 70°C and formaldehyde (7.6 g of 37% aqueous solution) added dropwise over a twenty minute period. The reaction was then stirred at 65-70° for an additional four hours. The mixture was cooled and the solid collected and susepnded in 400 ml of 1 *N* sodium hydroxide. The melting points and purification procedures for each diamine are given below.

DIAMINE	M.P. (RECRYSTALLIZATION SOLVENT)
4,4'-methylenebis(2-bromoaniline)	116-119°C (methanol)
4,4'-methylenebis(2,3-dichloroaniline)	251-254°C (*n*-butanol)
4,4'-methylenebis(2,5-dichloroaniline)	160-162.5°C (isopropanol/water)
4,4'-methylenebis(2,6-dichloroaniline)	254.5-255°C (acetic acid)
4,4'-methylenebis(2-nitroaniline)	239-245°C (crude)
4,4'-methylenebis(2-chloro-5-methoxyaniline)	104-110°C (crude)
4,4'-methylenebis(2,6-diethylaniline)	83-84°C (ethanol)

Table 25

PROPERTIES OF DIISOCYANATES

DIISOCYANATE	% NCO[1]	% HC[2]	BOILING POINT	MELTING POINT
2,6-Diethyl-*p*-phenylene	38.7 38.96 38.93	0.021 0.0017 0.029	104-105°C/0.3 mm 86°C/0.08 mm 89-90°C/0.05 mm	
3,5-Diethyl-4,4'-diisocyanatodiphenylmethane	27.04		172°C/0.33 mm	
2,6-Dimethyl-*p*-phenylene	44.1	0.0186	78°C/0.03 mm	58°C
2,4-Diethyl-*m*-phenylene	38.66	0.015	90°C/0.15 mm	
2,4-Dimethyl-*m*-phenylene	44.47	0.010	82°C/0.3 mm	
3,3',5,5'-Tetraethyl-4,4'-diisocyanatodiphenylmethane	23.67	0.0059	204°C/0.3 mm	52-54°C
3,3',5,5'-Tetramethyl-4,4'-diisocyanatodiphenylmethane				131°C
4,4'-Diisocyanatodiphenyl ether	33.5	0.137	158°C/0.15 mm	
4-Methoxy-*m*-phenylene	44.1	0.135	94°C/0.035 mm	
m-Xylylene	43.8	0.007	132-134°C/1.4 mm	

[1]Determined using ASTM D 1638
[2]HC, hydrolyzable chlorides, determined using ASTM D 1638

2. 4,4'-Methylenebis(2-trifluoromethylaniline). To a solution of 161.0 g (1.0 mole) of *o*-trifluoromethylaniline in 500 ml of glacial acetic acid and 85 ml of concentrated hydrochloric acid, 37.5 ml of 37% formaldehyde was added dropwise at room temperature over 95 minutes. The reaction was stirred at room temperature for five days and the precipitate separated by filtration. The precipitate was suspended in 750 ml water and the pH adjusted to 10 with cooling. The resultant solid was filtered off, dried and distilled to give 91.4 g (53%) of a white solid, b.p. 162-164°C/0.4 mm. An elemental analysis was obtained to determine purity since no end point could be detected in a nonaqueous titration (perchloric acid in glacial acetic acid).

Anal. calcd for: $C_{15}H_{12}F_6N_3$: C, 53.90; H, 3.62; N, 8.38.
Found: C, 53.98; H, 3.64; N, 8.37

D. PREPARATION OF DIAMINES FOR USE AS EPOXY CURING AGENTS

1. Preparation of Glycol Bis(*p*-nitrobenzoates). Toluene (400 ml) and *p*-nitrobenzoyl chloride (0.21 mole) were charged to a reaction flask. A catalytic amount of pyridine (2 ml) was added and the mixture heated to reflux (110°C). The glycol (0.10 mole) was added dropwise with stirring and the reaction was stirred at reflux temperature for an additional three hours, then cooled. Using 1,4-butanediol as the glycol a solid precipitated from the reaction solution on cooling. The solid collected and washed with ether. A portion of the solid was recrystallized from glacial acetic acid and its properties compared with those of the crude reaction product. The melting points (174°C) and IR spectra were identical.

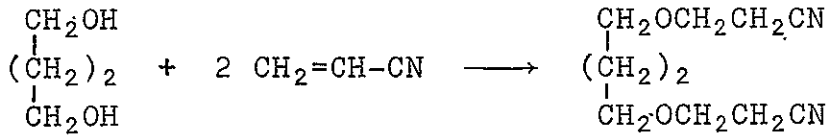
With triethyleneglycol a solid was obtained which had a melting point of 102.5-103°C.

When a 620 molecular weight polyoxytetramethylene glycol (Polymeg 620) was used, the solvent had to be removed on a rotary evaporator to obtain the pale yellow oily product.

2. Preparation of Glycol Bis(*p*-aminobenzoates). The bis-*p*-nitrobenzoate of triethyleneglycol and Polymeg 620 was dissolved in a ten-fold excess of THF and hydrogenated over Raney Nickel at 50 psi at 40°C. A solid product was obtained from the triethylene glycol based compound upon concentration of the THF. It was recrystallized from EtOH/THF (70/30). The melting point was 104.5°C. Titration gave a percent NH_2 of 8.07% (theoretical 8.20%).

The same general procedure, as shown above, was used with the Polyme 620 based compound, but in this case the product was liquid. Titration indicated an NH_2 content of 3.63% (theoretical 3.72%).

3. Cyanoethylation of 1,4-butanediol.



Trimethylbenzylammonium hydroxide (2.4 gm of 35% solution in methanol) and 1,4-butanediol (0.4 mole) were charged to a reaction flask fitted with a reflux condenser and a nitrogen purge. The solution was cooled to 19°C and cold acrylonitrile (3.15 moles) added dropwise with stirring. An ice bath was used to keep the temperature of the reaction flask below 30°C. After the addition was completed, the mixture was stirred for two hours and allowed to stand at room temperature overnight. The excess acrylonitrile was stripped off through a short Vigreux column attached directly to the reaction flask.

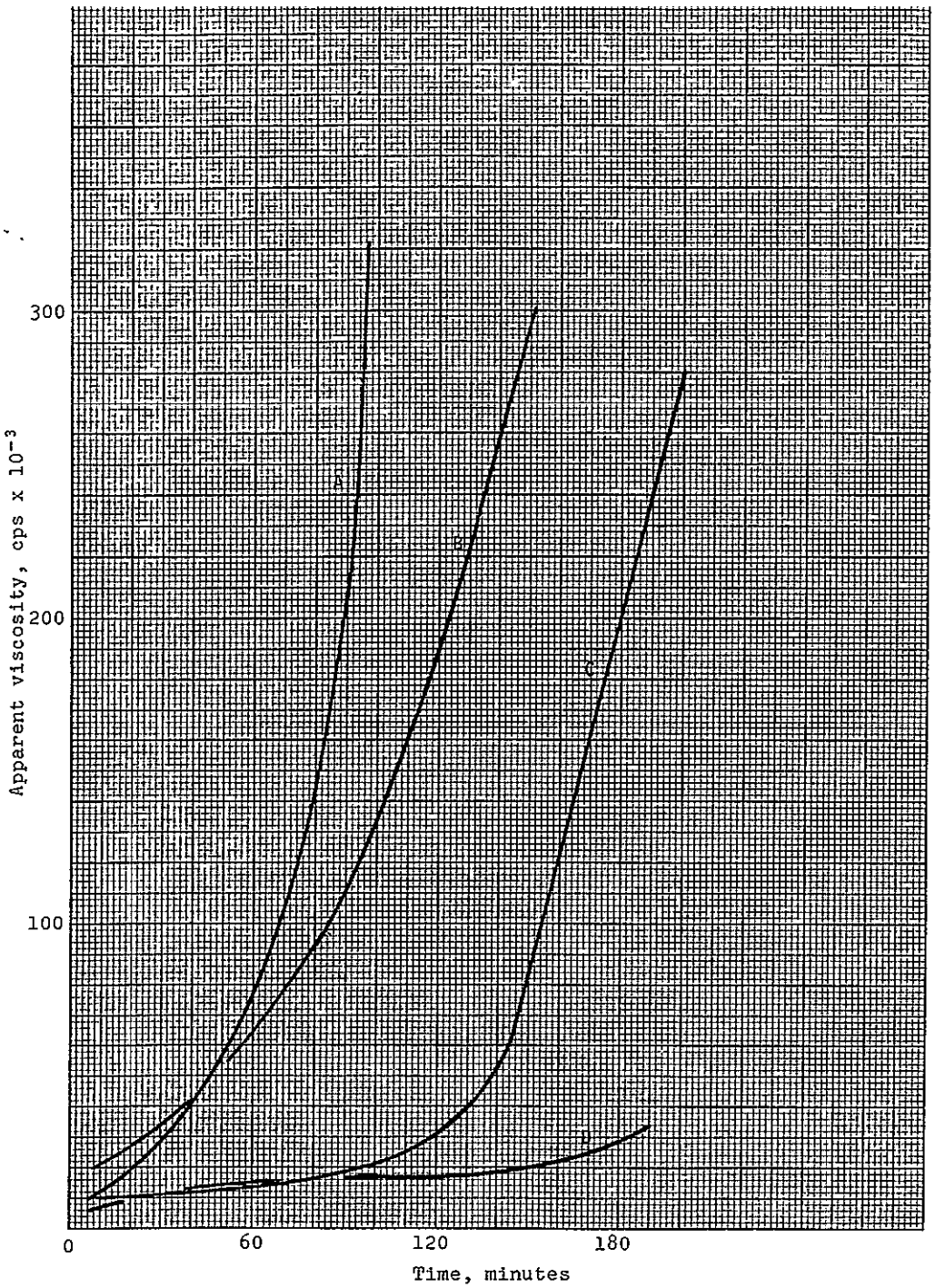
E. POLYURETHANE ADHESIVES POT LIFE DETERMINATION

The development of polyurethane adhesives, based on synthesized diisocyanates available in limited quantities, required that a method for estimating pot life be devised which used small amounts of the adhesive formulation. The following method has been employed to obtain pot life estimates. The pot life of MOCA-cured Adiprene L-100 was assumed to be one hour, and all other pot life estimates were taken relative to this figure.

A 10 by 75 mm test tube was filled to within one-half inch of the top with the adhesive formulation. The test tube was placed in a holder and raised into position centered around a number seven spindle (no disk) attached to a Brookfield viscometer (model HAF). The viscometer was run at 10 rpm and readings were taken at regular intervals. Zero time was designated as the point when the formulation was removed from the mixer, *i.e.*, three minutes after the molten MOCA had been added to the prepolymer. The readings were converted to viscosities using the appropriate factor. However, these viscosities can not be considered true viscosities due to the shape of the container. Figure 10 shows a plot of apparent viscosity versus time for four formulations. The pot life estimates were made based on this graph and known relative reaction rates taken from the literature.

F. WATER BREAK TEST

A glass eyedropper with an orifice of 0.060 inches is half filled with distilled water. Excess water at the orifice is removed with clean blotter paper. The dropper is held at 1.0 to 1.25 in. above the cleaned surface and one drop of water released. In order for



Curve	Sample	Prepolymer
A	81,591	2,4-Tolylene diisocyanate:Polymeg 1000 (2:1)
B	81,614	Adiprene L-100
C	81,602	2,6-Dimethyl-*p*-phenylene diisocyanate:Polymeg 1000 (2:1)
D	81,589	2,6-Diethyl-*p*-phenylene diisocyanate:Polymeg 1000 (2:1)

Figure 10. Viscosity versus Time for MOCA-cured Polyurethane Prepolymer

the surface to be considered satisfactorily clean, the water drop must spread to 1 in. diameter within two minutes (or cover the entire area in those cases where less than 1 in. of surface is available). The water drop can be removed with the point of a "Kim-wipe" prior to bonding the surface.

G. BONDING PROCEDURE

1. Surface Preparations.

a. Chromic Acid Etch. The metal (0.064 in. Alclad Aluminum 2014-T6, Federal Specification QQ-A-255), 1 in. x 3 in. panels, was cleaned with acetone or methyl ethyl ketone to remove all visible markings and dirt. After air-drying, the panels were vapor degreased in trichloroethylene. The degreased panels were then etched for 10 minutes at 70°C in the solution given below:

10 pbw	Sodium dihydrate
300 pbw	Distilled water
100 pbw	Concentrated sulfuric acid

After removal from the etching bath the panels were rinsed twice with distilled water and allowed to air-dry.

b. Chromic Acid Etch with Ferrous Sulfate Rinse. The aluminum was etched as above. After removal from the chromic acid bath, the aluminum was immersed in a 0.1 *N* ferrous sulfate bath at room temperature for 30 seconds. It was then rinsed thoroughly in running tap water followed by deionized water. The aluminum was then air-dried two hours prior to use.

c. Alkaline Cleaning Bath. The following treatment was used in some cases prior to the above two treatments. After vapor degreasing with trichloroethylene the aluminum was immersed in an alkaline cleaning bath for 10 minutes at 70°C. The composition of the bath was as follows:

sodium hydroxide	33.6 g
sodium pyrophosphate	56.3 g
sodium metasilicate	67.2 g
distilled (deionized) water	2850 ml

After removal from the bath the aluminum was rinsed in running tap water followed by deionized water.

2. Priming Techniques

a. Wipe Priming. A Kimwipe was saturated with the priming solution. It was then drawn across the aluminum surface, and the excess was immediately wiped off with a dry Kimwipe.

b. Spray Priming. The primer solution, contained in a Type EGA DeVilbiss air spray gun, was sprayed on the aluminum surface from 8 to 10 in. at 30 psi of nitrogen. An overlapping spray pattern was used to apply the solution as a fine mist. When using either priming technqiue, the primed metal was air-dried two hours prior to application of the adhesive.

3. Adhesive Application. The polyurethane adhesives were prepared by adding the curing agent in a liquid state to the pre-polymer at room temperature under nitrogen. The mixture was stirred slowly enough to prevent air entrapment using a marine type blade mixer, for three minutes when possible and then immediately applied to the aluminum. The lap shear specimens were prepared, using 1 in. x 3 in. x 0.064 in. aluminum specimens, in the jig shown in Figure 11 This jig permits a 0.5 in. overlap to be obtained automatically. All unboned areas were taped off using masking tape. The T-peel specimens were prepared, using 1 in. x 9 in. x 0.032 in. or 0.025 in. Aluminum specimens, in the jig shown in Figure 12. The bonded area was 6 inches. Glass beads, 6-7 mils in diameter, were used as spacers. Pressure, 2 to 5 pounds, was applied by means of lead weights.

H. PHYSICAL TESTING

The tensile shear strength determinations were carried out according to MIL-A-005090E testing procedure using an Instron tester. The T-peel strength determinations were done according to ASTM testing procedure D-1876.

The -196°C T-peel strengths were determined using a cryostat made from a block of polystyrene foam. A 4 in. x 10 in. x 11 in. cavity was cut in an 8 in. x 12 in. x 15 in. block, and a hole was provided for the reach-rod of an Instron testing machine. A metal drain tube and a polystyrene foam lid were also installed. The inner and outer walls were covered with a MOCA-cured Adiprene L-100 coating. The reach-rod and drain tube were sealed in with Dow Corning high vacuum silicone grease to prevent leakage of the liquid nitrogen. The cryostat inserted in the Instron is shown in Figure 13. The cryostat rests on the crosshead of the Instron and moves with it. This permits all joints to remain sealed throughout the test. After the test the liquid nitrogen is withdrawn into a Dewar to facilitate removal of the test specimen.

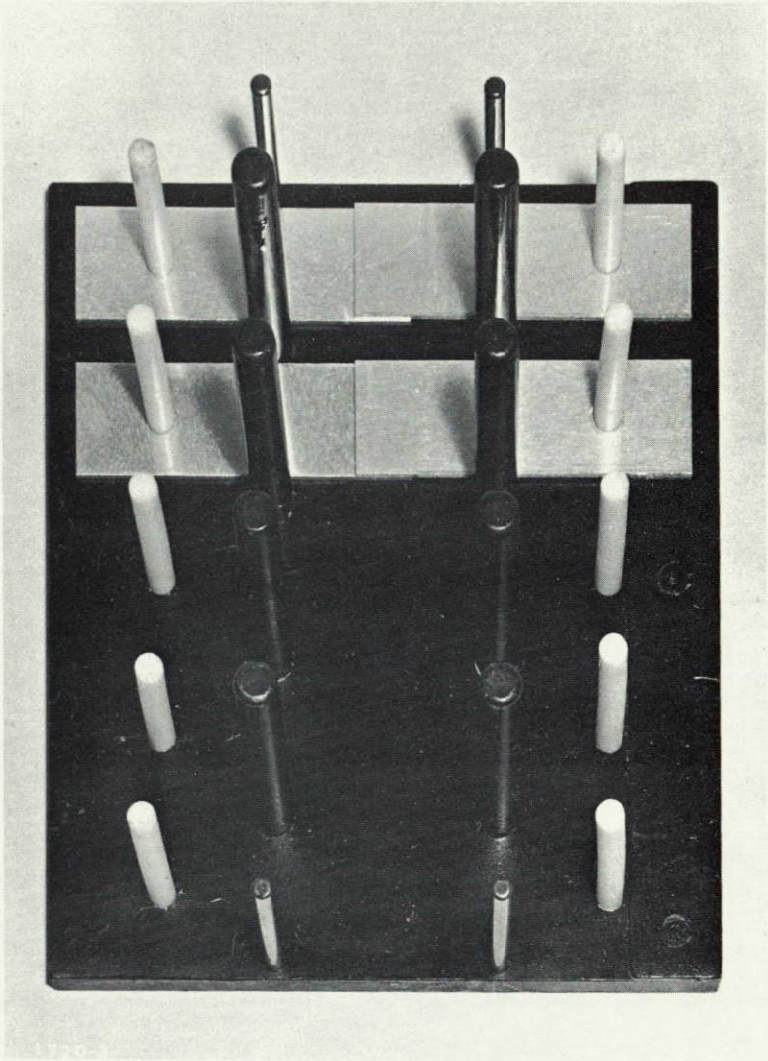


Figure 11. Lap shear specimen jig

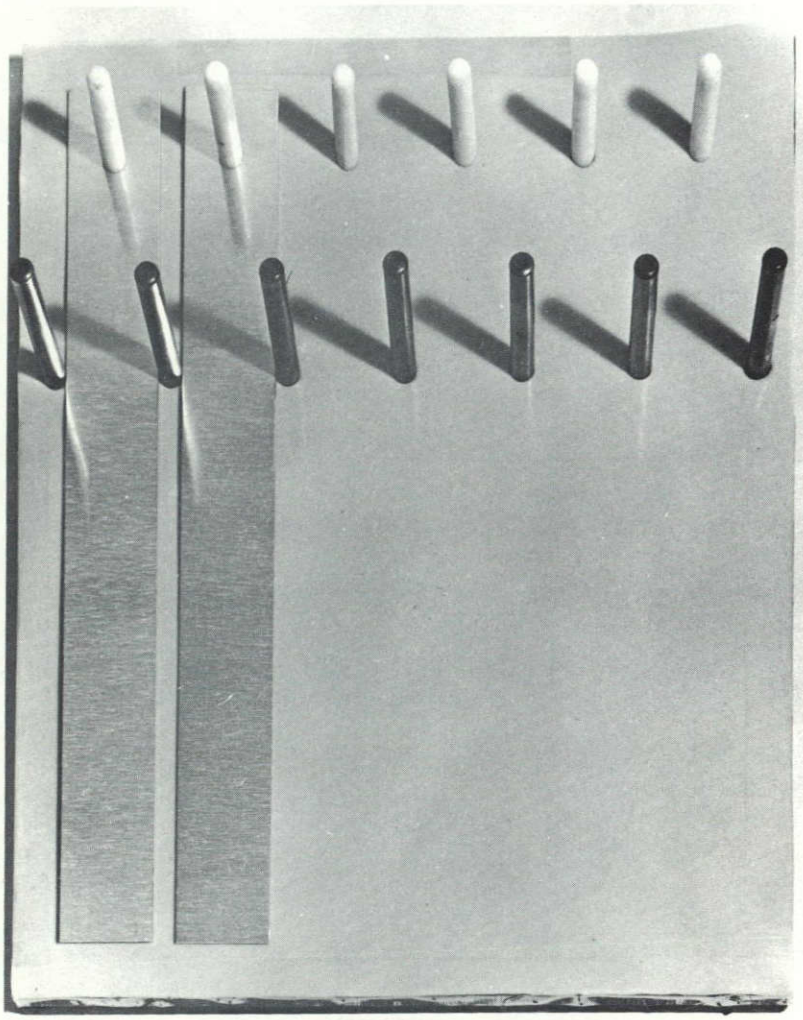
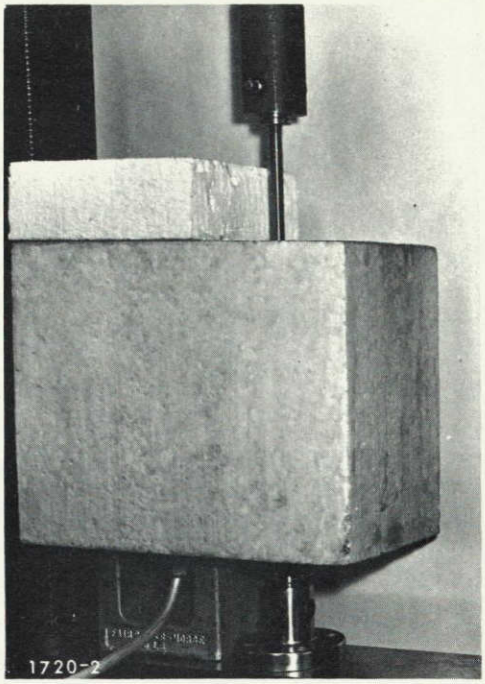
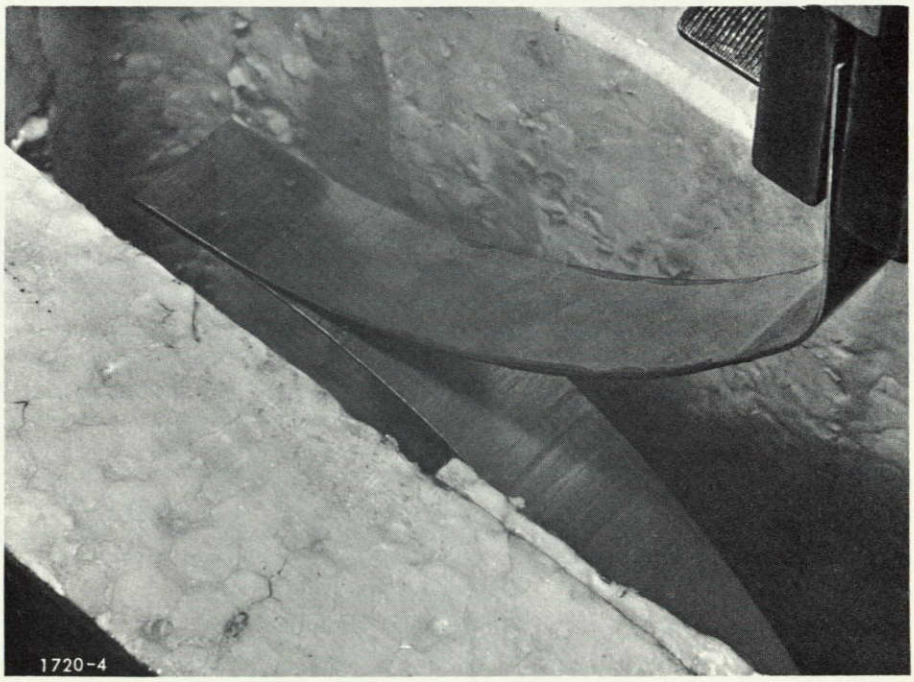


Figure 12. T-peel specimen jig



Cryostat for -196°C T-peel Strength Determinations



Interior of Cryostat with T-peel Specimen

Figure 13

The -196°C tensile shear strengths were determined by inserting the test specimens in a 6-oz polystyrene foam drinking cup, as shown in Figure 14. The test specimen was inserted through the cup and the hole sealed with silicone grease. The cup moves with the specimen, permitting retention of the seal throughout the test. Liquid nitrogen was added until boiling on the metal surface ceased, and then the tests were carried out.

The -269°C tensile shear strengths were determined in a Hofman Liquid Helium/Hydrogen Tensile Cryostat, Model HLHT, inserted in an Instron tester with the specimens immersed in liquid helium. Each end of the test specimens had two 1 in. x 1.5 in. reinforcing plates attached by spot welding. The cryostat is shown in Figure 15. The grip assembly used for holding the test specimen was designed and built by Monsanto Research Corporation. This proprietary grip design emphasized use of materials and construction to minimize heat losses yet permit rapid removal and insertion into the cryostat.

The Vicat softening temperatures were determined in accordance with ASTM procedure D-1525-58-T.

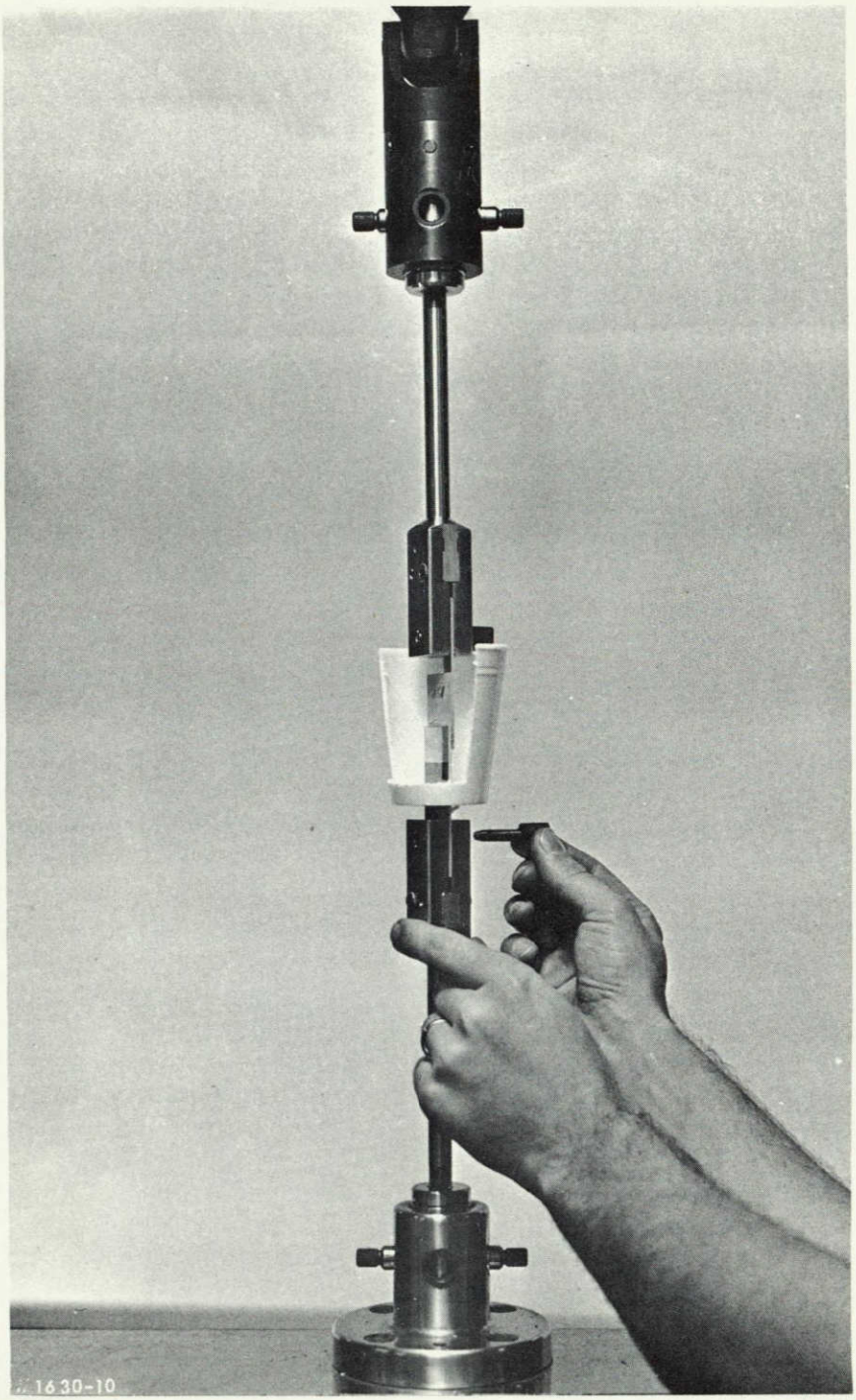


Figure 14. Cryostat for -196°C for tensile shear strength determinations

Figure 15. Hofman Liquid Helium/Hydrogen Tensile Cryostat, Model HLHT with windows

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